John T. Conway, Chairman
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DEFENSE NUCLEAR FACILITIES SAFETY BOARD

625 Indiana Avenue, NW, Suite 700, Washington, D.C. 20004
(202) 208-6400

March 5, 1997

The Honorable Thomas P. Grumbly
Under Secretary of Energy
1000 Independence Avenue, SW
Washington, DC 20585-1000

Dear Mr. Grumbly:

Defense Nuclear Facilities Safety Board (Board) Recommendation 96-1 expressed concern about benzene generation and release at the In-Tank Precipitation (ITP) Facility at the Savannah River Site. Members of the Board staff recently completed a technical evaluation of benzene generation, retention, and release at ITP. Their report, *Savannah River Site In-Tank Precipitation Facility Benzene Generation: Safety Implications,* evaluates the safety implications of these phenomena and assesses what should be understood about the processes before full-scale ITP operations proceed.

The Board shares the concerns expressed in this staff report. The Board again wishes to reemphasize the importance of developing an understanding of the physical and chemical mechanisms that cause the generation and release of benzene in operations at ITP, as conveyed in its Recommendation 96-1.

Sincerely,
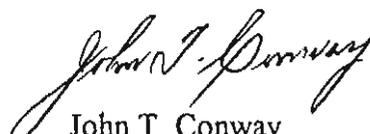
John T. Conway
Chairman

c: The Honorable Alvin L. Alm
Mr. Mark B. Whitaker, Jr.

Enclosure

SAVANNAH RIVER SITE
IN-TANK PRECIPITATION FACILITY
BENZENE GENERATION:
SAFETY IMPLICATIONS

Defense Nuclear Facilities Safety Board

Technical Report

February 3, 1997

SAVANNAH RIVER SITE
IN-TANK PRECIPITATION FACILITY
BENZENE GENERATION:
SAFETY IMPLICATIONS

This technical report was prepared for the Defense Nuclear Facilities Safety Board by the following staff members:

Randall Robinson
Joe Sanders
Lani Miyoshi
Kent Fortenberry
Roger Zavadoski

with advice from outside expert:

Julian Nichols

and former DNFSB staff member:

David Lowe

February 3, 1997

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EXECUTIVE SUMMARY

During November and December 1995, an unexpected excursion occurred in Tank 48 of the In-Tank Precipitation Facility at the Savannah River Site. Approximately 9,600 kilograms (kg) of excess sodium tetraphenylborate in 170,000 gallons of solution rapidly decomposed, generating a large amount of benzene at an unexpectedly high rate. Fortunately, the benzene was retained in the liquid slurry and was not immediately released into the vapor space.

It would appear that the benzene retention property of the Tank 48 slurry was the only barrier preventing a flammable concentration of benzene during this excursion. A deflagration of benzene vapor in Tank 48 of the In-Tank Precipitation Facility could produce radioactive exposures as high as 26 rem off site and 16,000 rem on site. To prevent such an event, controls for the Tank 48 headspace have been implemented to (1) restrict benzene and oxygen concentrations during normal operation of the Nitrogen Purge Ventilation System (ventilation system) and (2) restrict benzene concentrations during failure of the ventilation system. Although the allowable concentrations of benzene and oxygen were fortuitously maintained during this excursion, the high benzene release rates that ensued would have exceeded safety limits had the ventilation system failed.

An outside panel of experts (Process Chemistry and Mechanisms Panel) was established in January 1996 to guide an experimental program to determine the decomposition mechanism involved in the excursion. In April 1996, Westinghouse Savannah River Company duplicated the decomposition reaction in the laboratory using simulated waste and accelerated conditions (higher temperature and greater concentrations of metals that appear to catalyze the reaction). Although the experimental program has made progress, the mechanisms of the retention and release of benzene from the supersaturated solution remain poorly understood. This is of particular concern because as noted, it was not a design feature, but a fortuitous condition, that prevented the immediate release of the 8,500 kg of benzene generated in the 1995 excursion.

Effort is currently being made toward understanding the mechanisms and kinetics of benzene retention and release. Westinghouse Savannah River Company has formed an expert panel, similar to the Process Chemistry and Mechanisms Panel, to provide guidance in this regard. This panel initially convened in September 1996. Until the retention and release mechanisms are understood, Defense Nuclear Facilities Safety Board (Board) staff believe it would be prudent to avoid taking credit in subsequent safety bases for the retention of benzene in the tank liquid slurry.

Westinghouse Savannah River Company had planned near-term operation of the In-Tank Precipitation Facility for the purpose of verification testing. The near-term operation involved the addition of high-level waste supernate and sodium tetraphenylborate to Tank 48. This operation involved sizable quantities of material and was similar to a continuation of normal operations. To preclude a vapor explosion, controls on the allowable concentration of benzene and oxygen during normal operation of the ventilation system were to be implemented. Because of the

higher-than-expected benzene generation rate, limits on oxygen concentrations would have replaced the previous limits on benzene concentrations during conditions when the ventilation system was inoperable. While a number of additional modifications and upgrades were planned to support the development of an adequate safety basis for continuing full-scale operation of the In-Tank Precipitation Facility, Westinghouse Savannah River Company and DOE-Savannah River concluded that these modifications and upgrades were not necessary for the planned near-term operation. Recommendation 96-1 curtailed all near-term operations with the exception of a small process verification test, which introduced 300 gallons of sodium tetraphenylborate into Tank 48 to test cesium decontamination and filter processing.

Board staff believe that prior to Recommendation 96-1, Westinghouse Savannah River Company had not provided adequate technical justification for proceeding with near-term operation of the In-Tank Precipitation Facility. Specifically, the staff had two concerns:

- Because the mechanisms and bounding values for the rates of decomposition and benzene retention and release were not well understood, there is no assurance that the allowable benzene concentrations can be maintained during normal operation of the ventilation system. The maximum acceptable benzene release can be limited, however, by adding an equivalently small amount of tetraphenylborate.

- There is no assurance that the allowable oxygen concentrations can be maintained when the ventilation system fails because the current backup inerting system is not safety class, and the safety upgrades deemed necessary for long-term operation will not be in place.

As part of the review of Recommendation 96-1 Implementation Plan program deliverables, the Board staff will ensure that:

- The basic parameters that control the rate of benzene generation from the decomposition of tetraphenylborate will be determined.

- The mechanisms and bounding values for benzene retention and release will be determined.

- Measures, such as laboratory-scale tests of batch samples prior to waste or tetraphenylborate additions, that would limit excess tetraphenylborate additions and provide added assurance that benzene generation and release rates will remain within expected values will be identified.

- The modifications and other safety measures that are to be implemented prior to continued long-term operation of the In-Tank Precipitation Facility will be identified.

- Each such modification or safety measure that will not be implemented prior to the proposed near-term operation of the facility will be justified.

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1. INTRODUCTION

During November and December 1995, an unexpected excursion occurred in Tank 48 of the In-Tank Precipitation Facility at the Savannah River Site (SRS). Approximately 9,600 kilograms (kg) of excess sodium tetraphenylborate (NaTPB) in 170,000 gallons of solution rapidly decomposed, generating a large amount of benzene at an unexpectedly high rate. Fortunately, the benzene was retained in the liquid slurry and was not immediately released into the vapor space.

It would appear that the benzene retention property of the Tank 48 slurry was the only barrier preventing a flammable concentration of benzene during this excursion. A deflagration of benzene vapor in Tank 48 of the In-Tank Precipitation Facility could produce radioactive exposures as high as 26 rem off site and 16,000 rem on site. To prevent such an event, controls for the Tank 48 headspace have been implemented to (1) restrict benzene and oxygen concentrations during normal operation of the Nitrogen Purge Ventilation System (ventilation system) and (2) restrict benzene concentrations during failure of the ventilation system. Although the allowable concentrations of benzene and oxygen were fortuitously maintained during this excursion, the high benzene release rates that ensued would have exceeded safety limits had the ventilation system failed.

In a letter to the Department of Energy (DOE) (Conway, January 31, 1996), the Defense Nuclear Facilities Safety Board (Board) expressed concern about the unexpected chemical excursion in Tank 48. The Board stated: "No additional tank waste or sodium tetraphenylborate should be added to Tank 48 until the tetraphenylborate decomposition and benzene release mechanisms are well understood, adequate safety measures are in place, and appropriate changes are made to the ITP Authorization Basis."

DOE's reply (Guimond, March 1, 1996) stated: ". . . assurance of a complete understanding and control of the chemistry in the ITP process will be required prior to DOE authorizing further processing of high-level waste in ITP."

An outside panel of experts (Process Chemistry and Mechanisms Panel) was established in January 1996 to guide an experimental program to determine the decomposition mechanism involved in the excursion. In April 1996, Westinghouse Savannah River Company duplicated the decomposition reaction in the laboratory using simulated waste and accelerated conditions (higher temperature and greater concentrations of metals that appear to catalyze the reaction). Although the experimental program to develop understanding of the mechanisms governing decomposition of excess tetraphenylborate (TPB) has made progress, the mechanisms of the retention and release of benzene from the supersaturated solution remain poorly understood. This is of particular concern because as noted above, it was not a design feature, but a fortuitous condition, that prevented the immediate release of the 8,500 kg of benzene generated in the 1995 excursion.

Effort is currently being made toward understanding the mechanisms and kinetics of benzene retention and release. Westinghouse Savannah River Company has formed an expert panel, similar to the Process Chemistry and Mechanisms Panel, to provide guidance in this regard. This panel initially convened in September 1996. Until the retention and release mechanisms are understood, Board staff believe that in agreement with the Board's Recommendation 96-1, it would be prudent to avoid taking credit in subsequent safety bases for the retention of benzene in the tank liquid slurry.

Prior to Board Recommendation 96-1, Westinghouse Savannah River Company planned near-term operation of the In-Tank Precipitation Facility for the purpose of verification testing. This operation involved the addition of high-level waste supernate and NaTPB to Tank 48. The near-term operation involved sizable quantities of material and was similar to a continuation of normal operations. To preclude a vapor explosion, controls on the allowable concentration of benzene and oxygen during normal operation of the ventilation system were to be implemented. Because of the higher-than-expected benzene generation rate, limits on oxygen concentrations would have replaced the previous limits on benzene concentrations during conditions when the ventilation system was inoperable. While a number of additional modifications and upgrades were planned to support the development of an adequate safety basis for continuing full-scale operation of the In-Tank Precipitation Facility, Westinghouse Savannah River Company and DOE-Savannah River concluded that these modifications and upgrades were not necessary for the planned near-term operation. Recommendation 96-1 curtailed all near-term operations with the exception of a small process verification test, which introduced 300 gallons of NaTPB into Tank 48 to test cesium decontamination and filter processing.

The remainder of this report is organized as follows. Section 2 provides background information on the In-Tank Precipitation process and the process excursion. Sections 3 and 4 examine the issues of tetraphenylborate decomposition and benzene retention and release, respectively. Section 5 addresses the resumption of operations at the In-Tank Precipitation Facility. Section 6 presents a summary and conclusions. The report ends with two appendices, a list of references, and a glossary of acronyms and abbreviations.

2. BACKGROUND

This section provides background information on the benzene generation at the In-Tank Precipitation Facility. It describes the In-Tank Precipitation process, the original safety basis for Tank 48, Tank 48 testing during 1983-1995, the late-1995 process excursion in the tank, the resulting correspondence between the Board and DOE, deinventory operations following the excursion, and the investigation initiated by the excursion.

2.1 IN-TANK PRECIPITATION PROCESS DESCRIPTION

Large quantities of highly radioactive waste have accumulated at SRS through years of processing of nuclear materials in the 200 F- and H-Area separation facilities. Approximately 35 million gallons of high-level radioactive liquid waste with 500 million curies of primarily beta-gamma activity is stored in F- and H-Area tank farms. To minimize long-term risks to the public and the environment, the DOE is preparing to dispose of this waste permanently by vitrifying it at the Defense Waste Processing Facility at SRS. SRS is currently operated for DOE by Westinghouse Savannah River Company.

The In-Tank Precipitation Facility separates high-level waste (HLW) supernate from the SRS tank farms into HLW and low-level waste (LLW) fractions. The HLW fraction, along with radioactive sludge from the Extended Sludge Processing Facility, will be fed to the Defense Waste Processing Facility. The low-level decontaminated salt solution will be fed to the Z-Area Saltstone Facility, where it will be converted to a cemented waste form for on-site disposal in permanent vaults.

The average HLW contains sodium, potassium, and cesium in the ratio of 20,000:120:1. The TPB salts of sodium, potassium, and cesium have solubility products in the ratio $1:2.8 \times 10^{-8}:1.9 \times 10^{-9}$. Because of these ratios, decontamination factors for radioactive cesium (Cs-137) of approximately 30,000 can be attained using TPB. Thus, TPB was chosen as the precipitant for the In-Tank Precipitation process. To ensure that all the cesium is precipitated, excess TPB is added; the amount of excess TPB is calculated relative to the potassium concentration.

The primary components of the In-Tank Precipitation Facility include four liquid HLW tanks (the main process tank [Tank 48], the Defense Waste Processing Facility feed tank [Tank 49], the Saltstone feed tank [Tank 50], and the wash water tank [Tank 22]); the Filter Stripper Building; a control room; and a cold chemical feeds area.

The In-Tank Precipitation process is depicted in Figure 1. HLW supernate (dissolved salt solution) is added to Tank 48. NaTPB is added to the tank to precipitate cesium. Monosodium titanate (MST) is added to adsorb radioactive strontium, uranium, and plutonium. The slurry is concentrated by filtering. The material added and concentrated in one filtration cycle constitutes a

batch. Additional batches of HLW and NaTPB, but excluding MST, are added to the concentrated precipitate from previous batches. After three batches have been processed, the final slurry of approximately 10 weight percent solids is washed with water to dissolve the excess NaTPB and reduce the sodium concentration. Approximately 300,000 gallons of concentrated slurry is then transferred to Tank 49. Transfers from Tank 49 are made to the Late Wash Facility at the Defense Waste Processing Facility in approximately 5,000-gallon increments.
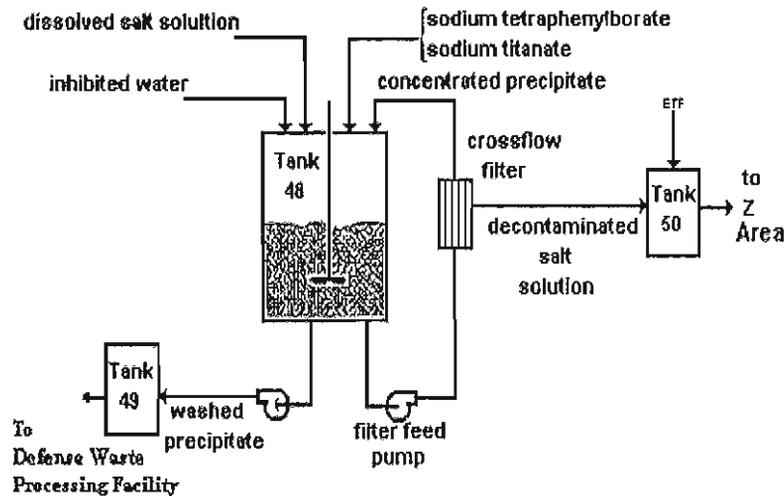

Figure 1. Process Flow Diagram of the In-Tank Precipitation Process

The filtrate from Tank 48 is stripped of benzene in the Filter Stripper Building and transferred to Tank 50. It is subsequently transferred to the Z-Area Saltstone Facility.

2.2   ORIGINAL TANK 48 SAFETY BASIS

The original safety basis for Tank 48 established the composite lower flammability limit (CLFL) to prevent a vapor deflagration during normal operation of the Nitrogen Purge Ventilation System. Control of oxygen in this mode of operation was provided as a defense-in-depth measure. The technical basis for Limiting Condition of Operation (LCO) 3.2.1 of the In-Tank Precipitation Operational Safety Requirements mandated that during this normal mode of operation, actual fuel concentrations be limited to 37 percent of CLFL and oxygen concentration be limited to 8 percent by volume (9 percent is the minimum oxygen concentration necessary to sustain a deflagration). Instrument uncertainties are incorporated into the measured limits of 25 percent of CLFL and 6.9 percent oxygen.

In case of failure of the Nitrogen Purge Ventilation System, the safety basis relied on controlling the CLFL. LCO 3.2.2 required that should normal ventilation be lost, at least 3 days must elapse before the CLFL is reached. Calculations supporting this requirement assume molecular diffusion as the sole mode of transport in the vapor space. The rationale for this

requirement is that the emergency purge ventilation equipment can be manually installed and operated within 3 days to ventilate the tank with air.

The original safety basis found the probability of a vapor deflagration in Tank 48 to be below the design basis frequency (less than 10^{-6} per year). The calculated off-site and on-site (100 meter collocated worker) consequences of such an accident are approximately 26 rem and 16,100 rem, respectively (Westinghouse Savannah River Company, May 23, 1994).

2.3   TANK 48 TESTING

2.3.1   Salt Decontamination Demonstration Test, 1983

In 1983, the first large-scale decontamination of HLW in Tank 48 was conducted. The purpose of this test was to verify, on an operational scale, the effectiveness of the TPB precipitation process for removing cesium. During the wash phase of the test, 183,000 gallons of water was added to the tank while the slurry pumps were operating. Benzene peaked at concentrations in excess of the maximum instrument reading for 6 hours. The technical analysis determined that the process had been successfully demonstrated, but recommended the causes of high benzene release rates and the quantity of benzene released be investigated (Heng, January 5, 1984).

Additional analysis of the benzene generation yielded three major conclusions—currently known to be incorrect. First, it was concluded that benzene was formed by predominantly radiolytic, rather than catalytic, decomposition of TPB. Second, the generated benzene was believed to have been transferred to one of two states: (1) free benzene, formed at a relatively constant rate in a given radiation field and immediately moving to the vapor phase, or (2) trapped benzene, formed at a higher rate and trapped in the crystalline structure of the slurry particles. Third, it was concluded that benzene trapped in the slurry particles was released as the solids dissolved during wash water additions. At that time, no correlation between the operation of the pumps and the benzene release was evaluated or identified.

2.3.2   Supplementary Testing Between 1983 and 1995

The postulated phenomenon of free and trapped benzene was observed experimentally at the University of Florida in the mid-1980s. This work resulted in the development of values for radiolytic production (G-values) for free and trapped benzene, respectively, of approximately 0.7 and 6.8 molecules decomposed per 100 electron volt (eV) of energy imparted. However, these tests were conducted under conditions different from those in Tank 48.

In 1987, additional testing was performed at Savannah River Technology Center under conditions similar to those in Tank 48, and the phenomenon of trapped benzene could not be duplicated to any significant extent. This issue was revisited in 1994 when additional testing

occurred at Savannah River Technology Center to support the development of the In-Tank Processing safety basis; these efforts included an attempt to refine the trapped benzene G-values. This testing again failed to reproduce trapped benzene under conditions similar to those in Tank 48. As a result, Georgia Institute of Technology was contracted to reproduce independently the phenomenon of trapped benzene. As in the testing at Savannah River Technology Center, significant trapped benzene was not observed in the Georgia Institute of Technology tests.

Between the 1983 test and 1995, no comprehensive analyses were completed to identify the mechanisms of benzene generation and release or to examine the potential effects on In-Tank Precipitation processing requirements. The research that was completed (1) continued to attribute benzene generation to radiolytic decomposition alone, (2) attributed the retention of the benzene in the slurry to a mechanism (crystalline entrapment) that could not be reproduced under conditions representative of those in the tank, and (3) only cursorily (and only in later studies) addressed potential release mechanisms other than those from washing operations.

2.3.3   Radioactive Operation Commissioning Test Program, 1995

The Radioactive Operation Commissioning Test Program began in September 1995, when 37,331 gallons of 0.55 molar NaTPB was added to Tank 48, which contained approximately 423,000 gallons of HLW solution, to precipitate cesium and potassium. During October and early November, the slurry was filtered, samples were taken, and testing was performed. Results from pump tests in October raised questions about the safety analysis contained in the In-Tank Precipitation authorization basis. Those tests showed the benzene release rate was a function of slurry pump operation (i.e., pump operation increased the benzene release rate). The benzene concentration in the tank vapor space increased to a measured peak of 60 parts per million (ppm) during the first pump run test. When the pumps were stopped, the benzene release decreased to the background level. The second and third pump run tests confirmed the results of the first; the peak measured benzene concentrations were 160 and 320 ppm, respectively. These benzene releases were much larger than those expected from radiolysis alone. However, they were still less than 3 percent of the CLFL and within the In-Tank Precipitation authorization basis. Steady-state benzene levels in the headspace increased with increasing pump speed and number of pumps running.

2.4   PROCESS EXCURSION

Following the third pump test, the plant conducted a high-temperature minimum oxygen for combustion (MOC) test and completed additional pump runs. A maximum bulk temperature of 52°C was reached. On December 1, 1995, all four slurry pumps were operated to mix the tank contents before a variable-depth sample was taken, even though recommendations against simultaneous operation of all four pumps had been documented in an earlier analysis of the 1983 test (Westinghouse Savannah River Company, November 11, 1994). During this agitation period, the flammable vapor concentration measured in the headspace increased rapidly to 10.5

percent of the CLFL. The slurry pumps were shut down to control the benzene release. If the ventilation system had failed during this period of pump operation—assuming molecular diffusion as the sole transport mechanism—a small, localized, benzene-rich layer at or above the CLFL concentration would have formed at the slurry-vapor interface in approximately 2 minutes. Thus, the benzene generation rates observed during this period were determined to exceed the In-Tank Precipitation authorization basis (at least 3 days before a flammable mixture develops), and an Unreviewed Safety Question was declared.

This release of benzene resulted from the decomposition of NaTPB that occurred sometime during the period of November 5–December 28, 1995. Evidence of this decomposition is exhibited in the sample results shown in Table 1. By December 18, cesium was resolubilizing, indicating all excess NaTPB had decomposed. Additionally, boron and phenol (both produced from the breakdown of TPB) concentrations dramatically increased above initial values. Furthermore, the small cesium concentration in the sample taken December 1, consistent with the November 5 sample, indicated that the reaction was proceeding, and excess NaTPB still existed.

Table 1. Tank 48 Samples

Sample Date[1,2]	Cs-137 (nCi/g)	Soluble Boron (mg/l)	Phenol (mg/l)
Nov. 5, 1995	<0.5	108	<10
Dec. 1 (8)	<0.5	392	850
Dec. 18 (28)	27	610	1800
Jan. 5, 1996 (7)	50	614	740
Jan. 12, (16)	71	616	730
Jan. 21 (22)	78	561	740
Jan. 26 (29)	62	588	820
Feb. 10 (12)	78	544	980
Feb. 23 (26)	114	504	1030
Apr. 13 (15)	344	533	1190
May 4 (8)	360	-	--
Jun. 2 (4)	256	478	1276
Jun. 28 (2 Jul.)	274	470	1358

[1]Dissolved benzene in solution was not measured.
[2]The date in parentheses indicates when the sample was filtered in the laboratory in order to measure the value of these parameters in solution.

The gross rate of decomposition was determined by dividing the amount decomposed by the duration of the decomposition. The duration of the reaction cannot be determined accurately; therefore, the reaction rate lower bound was estimated by assuming decomposition occurred over the entire period of November 5–December 28. The calculated lower bound is 12,500 micrograms/liter-hr (μg/l-hr). Figures 2 and 3 show the maximum period during which the excess NaTPB decomposed on a temperature and oxygen history map (Westinghouse Savannah River Technology Center, May 10, 1996).
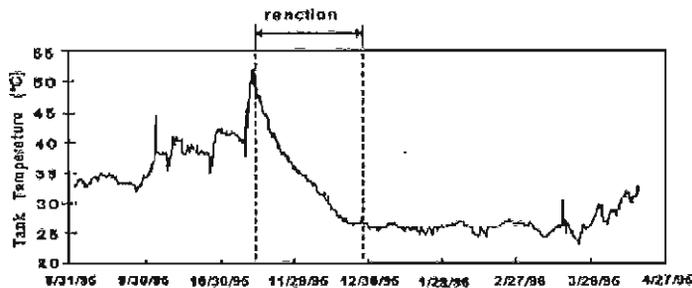

**Figure 2. Tank 48H Temperature History**
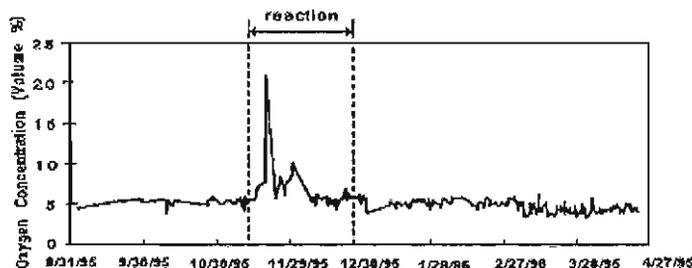
Figure 3. Tank 48H Oxygen History

There is substantial evidence that elevated temperature and/or elevated oxygen may have helped to initiate the process excursion. The maximum bulk temperature was 52°C, and the maximum oxygen concentration was 20 percent.

2.5   CORRESPONDENCE REGARDING THE EXCURSION

In a letter to DOE (Conway, January 31, 1996), the Board stated:

> . . . the immediate concern of a holdup of large amounts of benzene in Tank 48 must be dealt with in the near-term. The reliance on nitrogen inerting while the benzene is purged appears reasonable during the short period anticipated to reduce the benzene to low levels. However, controls should be in place to ensure that the benzene release rates are restrained to low levels (e.g., operate a single-slurry

pump until the benzene inventory is significantly reduced) and that flammable levels not exceed 25 percent of the lower flammability limit during pump operation. The Board understands that a Justification for Continued Operation (JCO) is being prepared for this operation. This JCO should also identify compensatory measures, such as enhanced management oversight, that will be in place during slurry pump operation.

No additional tank waste or sodium tetraphenylborate should be added to Tank 48 until the tetraphenylborate decomposition and benzene release mechanism are well understood, adequate safety measures are in place, and appropriate changes are made to the ITP Authorization Basis.

On March 1, 1996, DOE responded (Guimond, March 1, 1996):

. . . assurance of a complete understanding and control of the chemistry in the [ITP] process will be required prior to DOE authorizing further processing of high-level waste in ITP.

In essence, then, DOE is in agreement with the Board's position on the matter.

2.6 DEINVENTORY OPERATIONS

A JCO was approved on December 8, 1995, to address the Unreviewed Safety Question and allow continued operation of one slurry pump to deinventory benzene from Tank 48 (Westinghouse Savannah River Company, December 8, 1995). This JCO restricted the tank atmosphere to 10 percent of CLFL and 8 percent oxygen. Maximum benzene release rates to meet this restriction were calculated based on the capability to shut down the operating pump within 10 minutes of losing normal operation of the Nitrogen Purge Ventilation System. During operation under the initial JCO, benzene release rates were observed to be higher than anticipated after shutdown of the slurry pumps. Likewise, benzene releases observed with additions of water to the tank were above the limits imposed by the JCO. For these reasons, Tank 48 operations were again halted on January 3, 1996, and a need to revise the JCO was identified.

On February 13, 1996, DOE approved Revision 1 of a second JCO to permit controlled operation of the slurry pumps to remove excess benzene. This JCO used oxygen control (restricting oxygen concentration to 8 percent) rather than fuel control to ensure that the vapor space could be maintained nonflammable for 3 days upon loss of the normal Nitrogen Purge Ventilation System. To support this change, the Alternate Nitrogen System was installed to provide a small flow of nitrogen to the tank.

During the initial slurry pump run on March 5, 1996, higher-than-expected benzene generation rates and a resulting benzene concentration gradient from the liquid surface to the top of the tank were observed. As a result, the slurry pump was shut down after 14 minutes of operation. It was concluded that the CLFL limit in the Operational Safety Requirements (25 percent of the indicated CLFL) did not accurately portray concentrations in all areas of the vapor space because of the high benzene evolution rates and large concentration gradients near the fluid surface. This event resulted in Revision 2 of the second JCO. Revision 2 identified the sampling poles as safety related and required an LCO addition limiting benzene concentrations close to the liquid surface. In September 1996, the data from the March 5, 1996, pump runs were reviewed by an expert panel. The panel postulated that a stable, stratified vapor layer of benzene had formed prior to operation of the pumps. This vapor layer was the cause of the rapid rise in benzene vapor concentration in just 14 minutes of operation and the subsequent rapid decrease in vapor benzene concentration when the pumps were turned off. This event is discussed further in Section 2.7.

Benzene deinventory operations were reinitiated on March 8, 1996, and continued into May 1996. The majority of the benzene was removed from the tank during this period. Initially, one slurry pump was used. As benzene release rates decreased, additional slurry pumps were operated. Eventually, all four slurry pumps were operating, and the benzene release rate remained low. During the benzene depletion operations from December 1, 1995, to April 22, 1996, approximately 8,500 kg of benzene was removed.

Revision 3 of the second JCO, completed in April 1996, addressed the conduct of additional pump tests and inerting tests. The pump tests were designed to understand and verify benzene generation levels, and the inerting tests were designed to augment design data for a proposed safety-class Backup Nitrogen Purge System (Westinghouse Savannah River Company, April 1996). The inerting tests measure the rate of increase in Tank 48 vapor space oxygen concentration upon loss of inerting and determine the backup nitrogen purge rate required to keep fuel concentrations from reaching a flammable mixture after a loss of normal ventilation.

2.7   INVESTIGATION INITIATED BY THE PROCESS EXCURSION

When unexpected decomposition of soluble TPB was discovered, several experimental programs were initiated in an attempt to understand the chemistry and mechanism of the reaction (Westinghouse Savannah River Company, April 19, 1996). The Savannah River Technology Center tried to duplicate the reaction in Tank 48 using actual waste.

In January 1996, the Process Chemistry and Mechanisms Panel (Panel) was established to guide SRS through testing to determine the cause and mechanism of the decomposition of TPB. The Panel consists of experts in the fields of organic chemistry, organo-metallic chemistry, radiochemistry, and catalysis.[1]

The goal of the various experimental programs was to characterize the mechanism of benzene generation by understanding its phenomenology, stoichiometry, reaction mechanisms, and kinetics. The current understanding is briefly summarized in Section 3 of this report and in Appendix A.

Board staff have learned that a limited effort is being focused on the mechanisms and kinetics of benzene retention and release. Westinghouse Savannah River Company has recently established an expert panel, the Mass Transfer and Model Panel, similar to the Process Chemistry and Mechanisms Panel, to provide guidance in this area. However, this panel did not convene until September 1996. Analysis by the panel of the March 5 pump run data resulted in a postulation of an event first reported as possible in 1994 (Peterson, November 30, 1994). Peterson stated:

> Mixing of the vapor space in Tank 48 occurs primarily by natural convection. . . . Because the benzene has a higher molecular weight compared to air (78 versus 29) or water vapor (18), . . . it causes a stabilizing density gradient. . . . the density gradient due to concentration will cancel the gradient due to temperature, and natural convection will stop.

The measured time constant for decay of the vapor phase benzene after the pumps were stopped led to the postulation. Normally, the vapor phase is well mixed because of natural convection. When the pumps are stopped, the decay of benzene vapor concentration by dilution with nitrogen has a predictable half life of 4 hours. The March 5 pump run had a half life of 15 minutes, indicating the benzene vapor was not well mixed. The only viable conclusion is the vapor was stratified. Measurements made during the run indicate the stratified layer was not thicker than 1 foot. Based on benzene vapor pressure, the vapor concentration in the stratified layer was approximately 30 volume percent (300,000 ppm). Had the ventilation system (which has a history of tripping off an average of once per week) failed, Tank 48 would have been in a state where a deflagration was likely. Westinghouse Savannah River Company is also developing a mass transfer

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[1] The Panel members are as follows: Professor R. B. King, Chairman of the Department of Chemistry at the University of Georgia, expert in organo-metallic reactions and catalysis; Professor R. J. Hanrahan, University of Florida, expert in radiolysis and organic kinetics; Drs. G. W. Parshall and R. A. Smiley, retired DuPont employees, experts in catalysis and organic phenolic chemistry; Dr. N. M. Cole, expert in organic chemistry; and Dr. E. J. Lahoda, former SRS employee, Chair of the Panel, member of the High-Level Waste Review Committee, and an expert in chemical engineering, organic chemistry, and kinetics.

model to simulate benzene mass transfer conditions experienced in Tank 48, with and without slurry pump operation. While this will undoubtedly be useful in developing a bounding model, it will not explain how benzene is being retained, why release occurs at a much higher rate during slurry pump operation, and what other mechanisms might lead to a rapid release of benzene.

In addition to efforts initiated to understand TPB decomposition and release, full-scale tests in Tank 48 have proceeded to characterize the efficacy of the inerting system. Oxygen ingress during shutdown and low nitrogen purge were measured to support the safety inerting system upgrades. An experimental program was initiated at the Bureau of Mines to define the MOC over the range of benzene and hydrogen concentrations expected at the In-Tank Precipitation Facility, focusing on the range of 0–10 percent hydrogen relative to benzene. The results of these tests will be used to help define the functional requirements for the inerting conditions in Tank 48.

The lack of adequate understanding of the mechanisms of generation, retention, and release of benzene from the In-Tank Precipitation process, combined with the willingness of Westinghouse Savannah River Company to continue with the planned near-term operations in the face of these uncertainties, led to the Board's issuing Recommendation 96-1. Recommendation 96-1 states that except for Process Verification Test 1, no new waste or tetraphenylborate should be added to Tank 48 until an experimental plan has been completed to determine the cause of generation, retention, and release of benzene from the process. Recommendation 96-1 further requires that the knowledge gained from this experimental program shall be used to upgrade the safety basis for the facility.

3. TETRAPHENYLBORATE DECOMPOSITION

This section reviews the present status of understanding of TPB decomposition chemistry and the current program to understand decomposition rates and mechanisms.

3.1 STATUS OF UNDERSTANDING OF TETRAPHENYLBORATE DECOMPOSITION CHEMISTRY

Prior to the process excursion described in Section 2, the decomposition of excess TPB was attributed to radiolysis (Westinghouse Savannah River Company, November 11, 1994). Testing and analyses subsequent to the excursion have shown that the decomposition is catalytic on the soluble TPB⁻ ion. Copper and other metals not yet determined have been identified as the catalysts. The first successful demonstration of decomposition similar to the occurrence in Tank 48 was performed using simulated waste, elevated temperature, and increased copper concentration. The solubility of copper was found to be 2.0 ppm in the simulated waste. This measurement was consistent with the actual copper concentration of 1.5 ppm in Tank 48, demonstrating some representation of actual tank conditions.

Analysis of the decomposition reaction determined that the decomposition of TPB follows a series of steps from higher to lower phenolic content. The reaction could follow several pathways (one example: tetraphenylborate ⇀ triphenylboron ⇀ diphenylboron radical ⇀ phenylboronic acid ⇀ boric acid). Higher phenol yields were produced by aerobic conditions, whereas anoxic conditions produced higher benzene yields. The decomposition reaction proceeded immediately under anoxic conditions, but was delayed 100 hours by aerobic conditions. An incubation period may have been experienced in Tank 48 because the decomposition reaction did not initiate until approximately 2 months after the NaTPB was added. Changing conditions occurring before the decomposition reaction complicated the analysis of a possible induction period in Tank 48. Additional information on the chemistry of decomposition of TPB is included in Appendix A.

Testing has revealed that sodium sulfide (Na_2S) quenches the decomposition reactions, demonstrating (1) a potential method for controlling the decomposition rate and (2) the fact that decomposition of intermediates, which can continue after excess TPB has been eliminated, is also catalytic in nature. With this discovery of sulfide poisoning, the Process Chemistry and Mechanisms Panel concluded that the first step of decomposition is probably direct electron transfer from the cupric ion to the TPB⁻ ion in an aerobic atmosphere. Typical electron transfer reactions occur at rates approaching 10^{10} mole/liter-sec. Sodium sulfide prevents the electron transfer by precipitating the cupric ion to extremely insoluble copper sulfide. The rate-limiting steps of this reaction are probably diffusion and the rate of redissolution of NaTPB. Without the rate-limiting steps, the decomposition reaction would effectively occur instantaneously.

The amount of excess TPB added in September 1995 was higher than planned. Before the addition of TPB, the potassium measurements in the high-sodium background of the liquid ranged from 0.023 to 0.033 m. SRS chose the higher potassium level to calculate TPB excess. The actual potassium level appears to have been closer to the lower value, which resulted in the higher-than-planned TPB. As a result, when the TPB decomposed, a much larger quantity of benzene was generated than would have been the case if the actual potassium concentration had been measured more accurately. The high sodium levels in the waste caused most of the excess NaTPB to precipitate because of the common ion effect.

In a recent demonstration experiment run at Savannah River Technology Center for Process Verification Test Phase 1, Tank 49 material (essentially dilute TPB) was added to a sample of Tank 48 slurry at a temperature of 40°C. Prior to the addition, Cs-137 activity was 300 nanocuries per milliliter (nCi/ml). After the addition, the filtrate activity dropped to 3 nCi/ml, indicating that most of the Cs-137 had precipitated, and there was excess TPB present. Within 1 day, the excess TPB had decomposed, and the Cs-137 had increased to 534 nCi/ml. At 26 days after TPB addition, the Cs-137 had increased to 836 nCi/ml, nearly three times the preaddition value. This experiment disproved the hypothesis that cesium tetraphenylborate (CsTPB) and potassium tetraphenylborate (KTPB) precipitates are immune to rapid catalytic decomposition.

As a result of this experiment, the safety and effectiveness of the In-Tank Precipitation process are in doubt. There are a variety of potential catalysts in the HLW tanks that could degrade not only the excess soluble TPB, but also the desired precipitates. Attempting to control the amount of benzene available for release by minimizing excess TPB may no longer be viable. The results of this experiment indicate the entire inventory of TPB may be susceptible to rapid decomposition.

Few definitive conclusions can be drawn regarding the rates of the reactions leading to benzene generation. The initial decomposition rate is believed to be proportional to the amount of TPB⁻ ion present. The actual decomposition rate has a value within the range of 12,000 µg/liter-hr (time-averaged rate for the November 8–December 28 process excursion) to 9,100,000 µg/liter-hr (the highest rate observed in the laboratory).

3.2 CURRENT PROGRAM TO UNDERSTAND DECOMPOSITION RATES AND MECHANISMS

The prediction of the rate of benzene generation is obtained from the measured TPB reaction rates. The Panel recommended a "macroscopic" approach, that is, determining the maximum benzene generation rate within the capacity of the inerting system and controlling for that rate. To develop the necessary controls, bounding values of physically measurable and adjustable parameters correlating to that maximum rate must be determined.

Statistically designed tests varying the values of three parameters in stirred and vented vessels are currently under way. The purpose of these tests is to isolate the effects of temperature, catalyst concentration, and hydroxyl ion concentration on benzene generation. These tests are also being used to isolate rate constants for the chain of reactions. The current models use "lumped parameters" because the individual rate for each decomposing species is not well known. The model that best fits the actual tank data uses the following lumped equations:

$$NaTPB \underset{k_2}{\overset{k}{\rightleftharpoons}} Na^+ + TPB^-$$

$$TPB^- + Cu^+ \xrightarrow{k_3} [C_6H_6]_3 B + 0.88C_6H_6 + 0.12 byproducts$$

$$[C_6H_6]_3 B + Cu^+ \xrightarrow{k_4} [diphenyl\ products] + 0.88C_6H_6 + 0.12 byproducts$$

$$[diphenyl\ products] + Cu^+ \xrightarrow{k_5} [boron\ products] + 1.76C_6H_6 + 0.24 byproducts$$

$$TPB^- + [boron\ product] \xrightarrow{k_6} [C_6H_6]_3 B + 0.88C_6H_6 + 0.12 byproducts$$

$$k_5 = 2.5k_3$$

$$k_1 \gg k_3, k_4$$

$$E_A = 140 \frac{kJ}{mol}$$

$$k_3 \approx k_4$$
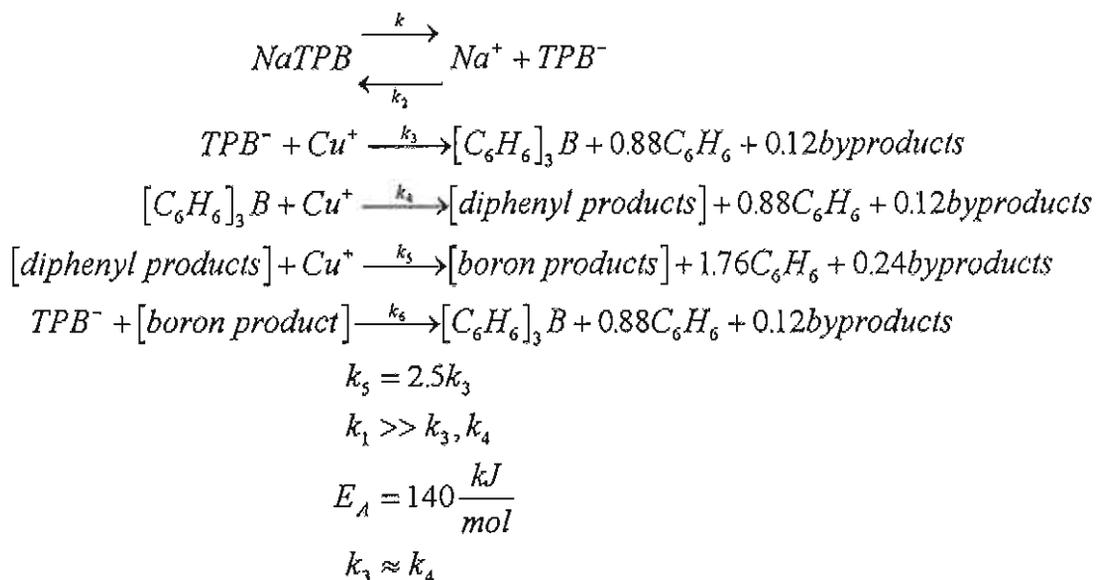
The model assumes catalytic initiation, coupled with autocatalysis by decomposition products (although laboratory tests have shown that autocatalysis does not occur) and catalytic decomposition of the intermediate products.

In addition, Pacific Northwest National Laboratories (PNNL) has been contracted to complete work in molecular modeling and nuclear magnetic resonance (NMR) measurement to help refine understanding of the decomposition reaction mechanism. NMR measurements will follow the boron intermediates as they progress through the reaction and identify free radicals formed; this process should provide rate estimates for the intermediate reaction steps. PNNL will also provide the necessary analytical methods for the high-pressure liquid chromatograph (HPLC) measurement of triphenylboron and the diphenylboron radical, the intermediates of the reaction.

The Panel also suggested additional testing under Tank 48 conditions and the continued study of sulfide poisoning through sulfide addition tests (with additions specifically near the peak generation rate) to further refine understanding of TPB decomposition. Moreover, the Panel recommended continued study to extract the rate constants for the slower decomposition of intermediate species.

4. BENZENE RETENTION AND RELEASE

This section reviews the potential mechanisms for benzene retention and release, and considers the safety implications of a limited understanding of those mechanisms.

4.1 POTENTIAL RETENTION AND RELEASE MECHANISMS

The phenomenon for retention of benzene in the Tank 48 slurry is not well understood. Board staff have seen no experimental verification of the mechanism for retention of benzene in the liquid phase. Possible retention mechanisms include adsorption, zeta potential effect, and surface tension. If the 8,500 kg of benzene released between December 1995 and April 1996 during deinventory activities had existed as free benzene in the liquid, its solubility would have been exceeded by a factor of six.

Although it has been demonstrated that tank slurry pump operation increases benzene release, the mechanism(s) for release are not known with certainty. Some possibilities are mechanical stripping of loosely adsorbed benzene by agitation; high localized temperatures in the pump, increasing the desorption rate; and oxygenation of the anoxic strata of the slurry.

Recent contact with DuPont's Sabine River Laboratory has confirmed their observation of a second benzene phase forming under the floating solid TPB precipitates. This second phase consists of a mixture of benzene and solids (a "rag" layer) remaining submerged in the liquid phase. No information is available about the stability of the rag layer or what might cause the benzene to release from the solids and form a floating pure benzene phase. If this were to happen, the vapor phase would be limited only by the vapor pressure of benzene, could quickly overwhelm the existing inerting system, and would form a flammable mixture.

4.2 SAFETY IMPLICATIONS OF POORLY UNDERSTOOD MECHANISMS

It was possible to control the benzene release rate from the slurry by operating from one to four Tank 48 slurry pumps under controls established by the JCOs. The maximum release rate experienced during benzene depletion activities was approximately 184 grams (g)/min. If benzene had been released immediately as it was produced and the decomposition rate had reached 30,000 µg/liter-hr (assuming 160,000 gallons and a purge flow rate of 750 standard cubic feet per minute [scfm]), the bulk vapor space of Tank 48 would have reached the CLFL in 6.8 hours even with normal operation of the Nitrogen Purge Ventilation System.

Appendix B provides calculations for the minimum benzene release rate that would lead to the CLFL (assuming a long period of release) and for the time to reach the CLFL for a release rate higher than that minimum value. Those calculations assume no initial benzene

concentration. Figure 4 provides a graph of the time required to reach the CLFL for various benzene generation rates (with no retention), given a slurry volume of 300,000 gallons and purge flow rates of 300 scfm (design minimum) and 750 scfm (typical system flow rate). From these calculations, it is clear that the retention of the benzene in the slurry was fortuitous.

Time to CLFL

$G(300)_\infty = 10,380\ \mu g/l \cdot hr$
$G(750)_\infty = 25,950\ \mu g/l \cdot hr$
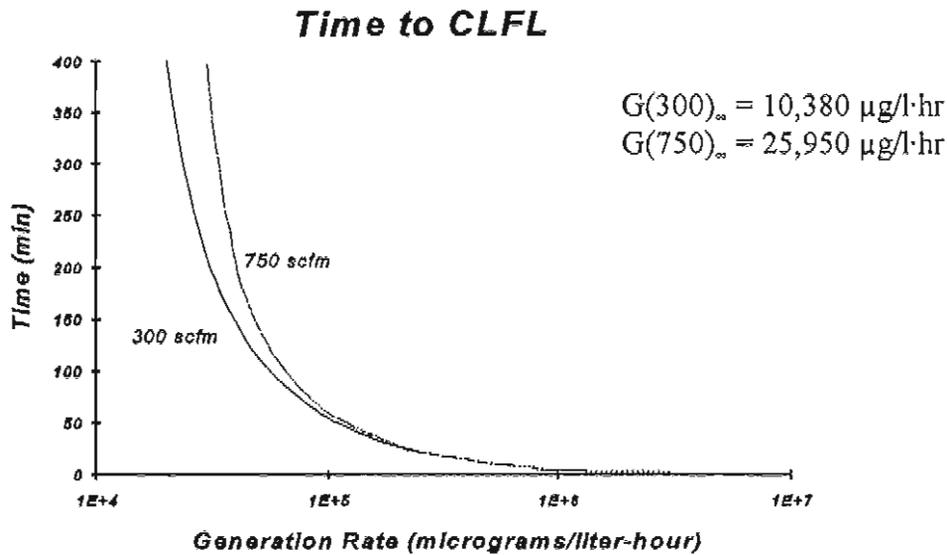
Figure 4. Calculated Time to CLFL

Board staff believe that the benzene retention property of the solids was the only barrier to a flammable concentration of benzene during the process excursion. A more limiting case might involve another method for the release of benzene other than pump operation. For example, the benzene could be released with the use of a surfactant if the benzene were held by surface tension with solids in the liquids.

As discussed in Section 2, research into the retention and release mechanisms remains in its preliminary stages. Until the mechanisms are well understood, repeatable on a process scale, and sufficiently controllable, it would be prudent to avoid taking credit for the retention of benzene in the slurry in subsequent safety bases.

5. RESUMPTION OF OPERATIONS

This section describes the near-term and long-term plans for operating the In-Tank Precipitation Facility and their safety implications.

5.1 NEAR-TERM OPERATION

5.1.1 Proposed Operation

Following completion of the inerting tests, Westinghouse Savannah River Company planned to begin near-term operation of the In-Tank Precipitation Facility for process verification testing. The testing involved two phases. Phase 1 activity was started in November 1996 and included adding approximately 300 gallons of 0.5 molar NaTPB to Tank 48, which separated and concentrated cesium by reprecipitating and filtering. The proposed Phase 2 activities, halted by Recommendation 96-1, would have included adding approximately 450,000 gallons of radioactive liquid supernate to Tank 48, precipitating cesium with a small excess of NaTPB, and concentrating the slurry by filtering.

5.1.2 Authorization Basis

The compensatory measures and controls necessary for near-term operation have not yet been fully identified by Westinghouse Savannah River Company or approved by DOE-Savannah River. Westinghouse Savannah River Company is in the process of developing a safety evaluation to support near-term operation. DOE-Savannah River has stated that the safety analyses encompassed by that evaluation will be more comprehensive than the JCOs that were approved to allow the expeditious removal of the large amount of benzene in Tank 48. The safety controls envisioned for near-term operation will be similar to those implemented for the benzene remediation operations, and will include continued reliance on the Alternate Nitrogen System and vapor space gas sampling poles.

A safety measure that could be incorporated into the safety basis would be limiting the excess TPB that could be added for the precipitation of potassium and cesium. The bounding rate of benzene released for each addition of HLW and TPB to the tank could be determined by conducting laboratory-scale tests with actual material at Savannah River Technology Center before performing this activity at the In-Tank Precipitation Facility. However, there are a number of conditions that may not be repeatable in the laboratory, but could significantly change the rate of decomposition of TPB, benzene retention, and the rate of release of benzene: (1) tank mixing (and its associated release rate), (2) the potential for localized high temperatures during that mixing, and (3) anoxic conditions deep in the tank versus aerobic conditions near the surface. Other possible measures for controlling potentially unsafe conditions are discussed in Section 6 of this report.

5.1.3 Safety Justification

Board staff view the planned near-term testing as comparable to the continuation of normal operations because additional tank waste and TPB will be added to Tank 48 (though in smaller quantities), and a formal test plan has not been developed. A formal test plan would be expected to provide a compelling argument that the information received from the tests will resolve In-Tank Precipitation Facility safety or operational issues. Additionally, the Defense Waste Processing Facility salt processing operations and Late Wash Facility are being readied for startup in late summer 1996, and In-Tank Precipitation Facility feed is required to support these operations. Near-term operation of the In-Tank Precipitation Facility will provide that feed.

A number of upgrades are envisioned to support development of the safety basis for continuing operations following the completion of the process verification tests. These upgrades are discussed in Section 5.2 below. They include (1) installation of a safety-class backup nitrogen purge system, (2) installation of new redundant oxygen analyzers (with less instrument uncertainty) in separate risers, (3) automatic isolation devices for loss of ventilation on various tank openings, and (4) installation of both hardware and software interlocks to shut off operating slurry pumps automatically upon loss of ventilation. The rationale for starting near-term operations without these upgrades has not been developed.

The immediate need to place Tank 48 into a safe condition by depleting the benzene inventory has been met. Acceptance of the increased risk associated with the use of compensatory measures and an interim safety basis was appropriate to that need. Board staff believe that DOE-Savannah River has not provided sufficient technical justification or demonstrated adequate understanding of the TPB decomposition and benzene generation and release mechanisms to warrant acceptance of the same increased risk for near-term operation.

5.2 LONG-TERM OPERATION

The modifications, compensatory measures, and procedures required to limit the rate of benzene evolution and ensure that the tank vapor space will remain inerted under all conditions have not been fully identified by Westinghouse Savannah River Company for either the proposed limited operation of the In-Tank Precipitation Facility for process verification testing or continued long-term operation. Table 2 summarizes the safety measures being considered by Westinghouse Savannah River Company to limit the rate of generated benzene and ensure that the tank vapor space remains inerted. Noted in the table are those modifications and measures that seem feasible for near-term operation of the facility and those upgrades envisioned by Westinghouse Savannah River Company as necessary to support development of an adequate safety basis for continued long-term operation.

Table 2. In-Tank Precipitation Facility Modifications and Other Safety Measures to Limit Benzene Generation and Release

Objective	Description	Comments
Limit rate of benzene generation	Limit the size of batches processed.	A limit on batch size could be implemented in the short term.
	Perform laboratory-scale testing at Savannah River Technology Center with a sample of actual material to be processed to bound the rate of benzene release prior to processing of the batch represented by the sample.	This laboratory test of different batch compositions could be implemented in the short term until a fuller understanding of the effect of slurry composition on benzene generation rate is achieved.
	Administratively limit the maximum amount of excess TPB added to Tank 48. Analyze the concentration of potassium to determine the amount of TPB required.	The concentration limit could be imposed in the short term, but the impact of decontamination factors for cesium would have to be monitored. Furthermore, measurement of the potassium cation concentration could be improved.
	Administratively limit the maximum Tank 48 slurry temperature.	This temperature limitation could be set in the short term, but could impose a more severe limit on batch size.
	Develop a more accurate method to determine the potassium concentration in the HLW.	The excess TPB is based on potassium concentration. Improving the accuracy of measuring this ion would allow the process to operate with a smaller tolerance of excess TPB.
	Add Na_2S to poison the catalyst for the decomposition of TPB.	The potential for stopping the generation of benzene by the addition of Na_2S appears very promising. However, considerable work will be needed to establish the required concentration and to ensure that this addition will not adversely affect In-Tank Precipitation Facility operation.
Ensure that tank vapor space remains inerted	Install a non-safety-class backup nitrogen purge system that is redundant to the currently installed system.	This capability was provided for the operations conducted to deplete the benzene inventory in Tank 48. However, it may not provide an adequate safety level for continued operation of the In-Tank Precipitation Facility.
	Administratively limit the maximum Tank 48 slurry temperature.	This temperature limitation could be set in the short term, but could impose a more severe limit on batch size.
	Install software and hardware interlocks on Tank 48 that would stop all slurry pumps upon loss of ventilation.	Software interlocks appear more feasible for the short term. Implementation of hardware interlocks may require more time.
	Install new redundant oxygen analyzers with less instrument uncertainty.	This modification appears feasible for the long term.

Table 2. In-Tank Precipitation Facility Modifications and Other Safety Measures to Limit Benzene Generation and Release (concluded)

Objective	Description	Comments
Ensure that tank vapor space remains inerted (concluded)	Implement a permanent sampling capability that can automatically provide rapid analyses of the Tank 48 vapor space at elevations from near the liquid surface to the top of the tank.	This modification is essentially an adaptation of sampling probes and gas chromatograph analysis capability used in the depletion of the benzene inventory in Tank 48.
	Provide automatic isolation of tank openings upon loss of ventilation.	This modification appears feasible for the long term.
	Provide a safety-class backup nitrogen purge system similar to the system at the Defense Waste Processing Facility. Consider including the capability to inject nitrogen near the liquid interface.	This modification may be required to provide adequate assurance that vapor space inerting is maintained under all conditions of operation.

6. SUMMARY AND CONCLUSIONS

Board staff believe that the benzene retention property of the Tank 48 slurry was the only barrier preventing a flammable concentration of benzene during the process excursion in late 1995. Recent operations to place Tank 48 into a safe condition by depleting this retained benzene inventory are now complete. The increased risk associated with depleting the benzene inventory was appropriate because of the immediate safety need involved.

Board staff also believe Westinghouse Savannah River Company, prior to Recommendation 96-1, had not provided adequate technical justification for acceptance of the same increased risk for near-term operation of the In-Tank Precipitation Facility. The proposed near-term operation of the facility would have involved the addition of HLW supernate and TPB to Tank 48. Board staff had two concerns about these operations:

- Because the mechanisms and bounding values for TPB decomposition and benzene retention and release are not well understood, there is no assurance that the allowable benzene concentration can be maintained during normal operation of the ventilation system. The maximum acceptable benzene release can be limited, however, by adding an equivalently small amount of TPB.

- There is no assurance that the allowable oxygen concentrations can be maintained when the ventilation system fails because the current backup inerting system is not safety class, and safety upgrades deemed necessary for long-term operation are not in place.

As part of the review of Recommendation 96-1 Implementation Plan program deliverables, the Board staff will ensure that:

- The basic parameters that control the rate of benzene generation from the decomposition of tetraphenylborate will be determined.

- The mechanisms and bounding values for benzene retention and release will be determined.

- Measures, such as laboratory-scale tests of batch samples prior to waste or tetraphenylborate additions, that would limit excess tetraphenylborate additions and provide added assurance that benzene generation and release rates will remain within expected values will be identified.

- The modifications and other safety measures that are to be implemented prior to continued long-term operation of the In-Tank Precipitation Facility will be identified.

- Each such modification or safety measure that will not be implemented prior to the proposed near-term operation of the facility will be justified.

APPENDIX A.   TETRAPHENYLBORATE CATALYTIC DECOMPOSITION

Results from testing at Savannah River Technology Center strongly support the conclusion that the inventory of excess tetraphenylborate in Tank 48 decomposed catalytically in the 1995 process excursion. The small amounts of copper and other unidentified metals in the slurry appear to have been the catalysts. Furthermore, there is significant evidence in the published literature and from testing at the center that the initiating reaction is a fast electron transfer from Cu^{++} in the reaction (Barnes, 1991):

$$(C_6H_5)_3 \ B(C_6H_5)^- + Cu^{++} \rightarrow (C_6H_5)_3 \ B(C_6H_5)^{\bullet} + Cu^+ \qquad (1)$$
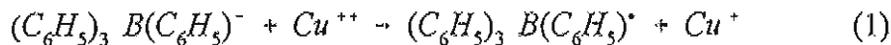
Reaction (1) can occur very rapidly (on the order 10^{10} mole/liter-sec). However, the rate during the 1995 excursion was probably limited by the rate of dissolution of NaTPB; otherwise, the decomposition reaction would have occurred nearly instantaneously. Reaction (1) occurs in both anoxic (oxygen-starved) and aerobic conditions. The next reaction step depends on whether the environment is aerobic or anoxic. If oxygen is present, the following Cu^{++} - Cu^+ redox couple is established:

$$4Cu^+ + O_2 \rightarrow 4Cu^{++} + 2O^{--}$$

$$2O^{--} + 2H_2O \rightarrow 4OH^- \qquad (2)$$
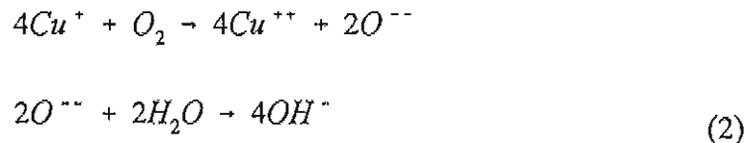
This reaction allows the Cu^{++} to react with more TPB$^-$, providing the catalytic effect. Once reaction (1) takes place, the intermediates decompose stepwise to benzene and byproducts, as discussed by Barnes (1991). The catalyst must be constantly regenerated to its reactive form in a scheme similar to reaction (2) for a small amount of the catalyst (copper) to effectively decompose 10,000 times its own weight or more.

In anoxic conditions, catalysis with copper may occur as follows:

$$(C_6H_5)_3 \ B(C_6H_5)^- + Cu^+ \rightarrow (C_6H_5)_3 \ B(C_6H_5)^{\bullet} + Cu \qquad (3)$$
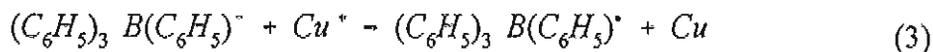
While there is evidence of reaction (3), no mechanism has been identified for the reoxidation of Cu or Cu^+ to Cu^{++} to complete the catalytic effect. If the decomposition were to proceed with reaction schemes (1) and (3), the copper would be consumed and could not act as a catalyst. Tests conducted under anoxic conditions have verified the catalytic effect, suggesting that another mechanism for regenerating copper to its reactive form is likely. A complex scheme of intermediate decomposition steps involving Cu^+ and the various phenolic compounds has been proposed, but cannot be proven without NMR techniques. PNNL has been contracted to do this work.

The proposed mechanisms for aerobic decomposition are shown in Figure A-1. The aerobic reaction scheme is better understood than the anoxic reaction scheme since most of the testing identified in the literature was performed in air. In aerobic conditions, once decomposition starts and phenylboronic acid (PBA) is formed, a second cycle of reaction with the TPB begins. The slow decomposition of PBA forms boric acid that supplements Cu^{++} in decomposing the excess TPB. The diphenylboron and phenyl radicals undergo dimerization, oxidation, and alkaline-adduct hydrolysis to form diphenylboron, phenol, PBA, benzene, and the diphenylboron dimer.
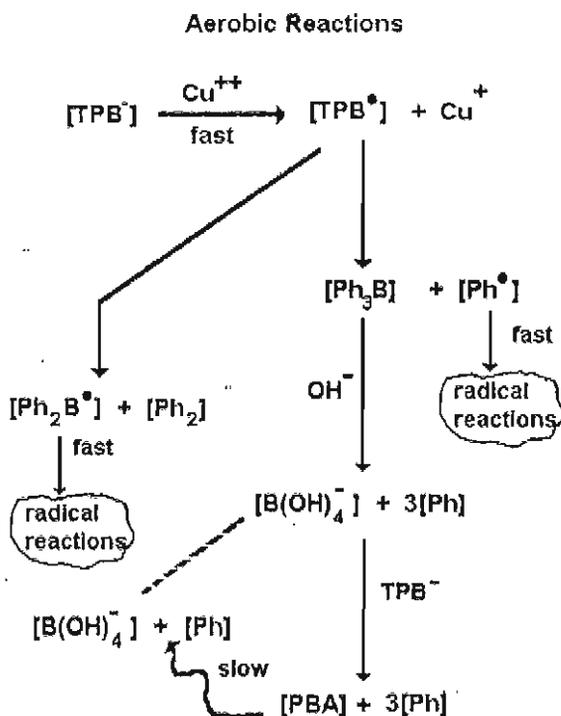
Aerobic Reactions

Figure A-1. Aerobic Decomposition Reaction Scheme

In the anoxic reaction scheme, Cu^{++} decomposes TPB into two species: (1) the TPB radical and (2) the Cu(I)-salt of TPB. The TPB radical decomposes by the same pathways as the aerobically produced radical. The Cu(I)-salt of TPB undergoes a series of steps releasing benzene and Cu^+. Cu^+ is available to react with TPB to form Cu(I)-salt of TPB to restart the same sequence of reaction steps.

The proposed reaction sequence for anoxic decomposition is shown in Figure A-2. Anoxic conditions produce higher yields of benzene than do aerobic conditions.
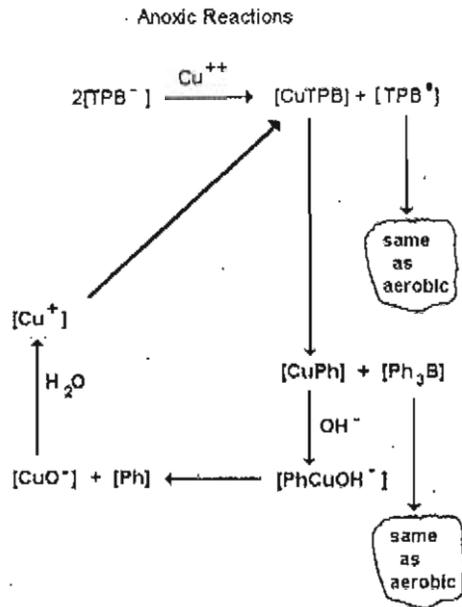
Figure A-2. Anoxic Decomposition Reaction Scheme

The role of oxygen in the decomposition reaction not only determines the yields of benzene versus phenol, but also plays an important role in the characteristics of the reaction. This can be illustrated by examining the data obtained from the two laboratory tests that duplicated the reaction in Tank 48. Figure A-3 is a plot of reaction rate with time in a stirred aerobic tank in contact with simulated nonradioactive waste at 70°C and 10 ppm copper (only 1.99 ppm solubilized). An incubation period of approximately 100 hours was observed before the decomposition reaction proceeded; a maximum rate of 2,000,000 μg/liter-hr was observed. The yields of the aerobic reaction were predominantly benzene (90 percent) and phenol (9 percent). An incubation period was also observed in Tank 48, but the relative phenol yield was smaller.

The experimental results for the anoxic decomposition reaction, shown in Figure A-4, reveal that the decomposition reaction proceeded instantaneously. The yield from this reaction was 99 percent benzene, similar to the yield obtained in Tank 48. Thus, the reaction in Tank 48 seems to have exhibited both aerobic and anoxic behavior. The yields resembled those from anoxic conditions, while the incubation period experienced suggests aerobic conditions.
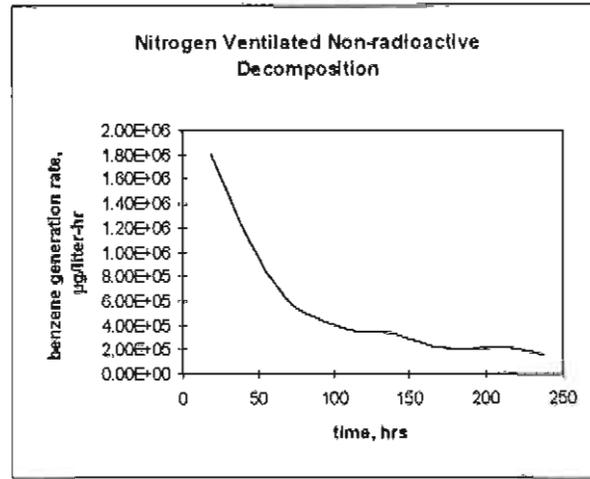
Figure A-3. Air-Ventilated TPB Decomposition in Contact
with Simulated High-Level Waste at 70°C
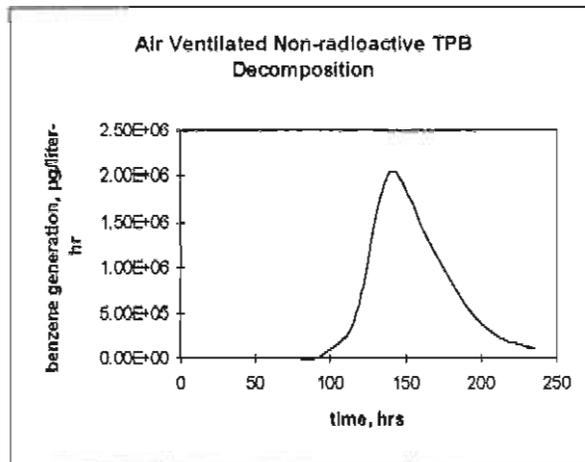
Figure A-4. Nitrogen-Ventilated TPB Decomposition in Contact
with Simulated High-Level Waste at 70°C

APPENDIX B. ILLUSTRATION OF THE APPROACH TO COMPOSITE LOWER FLAMMABILITY LIMIT WITH NORMAL PURGE VENTILATION SYSTEM OPERATION

C : benzene concentration as a function of time $(\frac{moles}{ft^3})$

F : purge flow rate $(\frac{ft^3}{hr})$

V : vapor space volume (ft^3)

G : benzene release rate $(\frac{moles}{hr})$
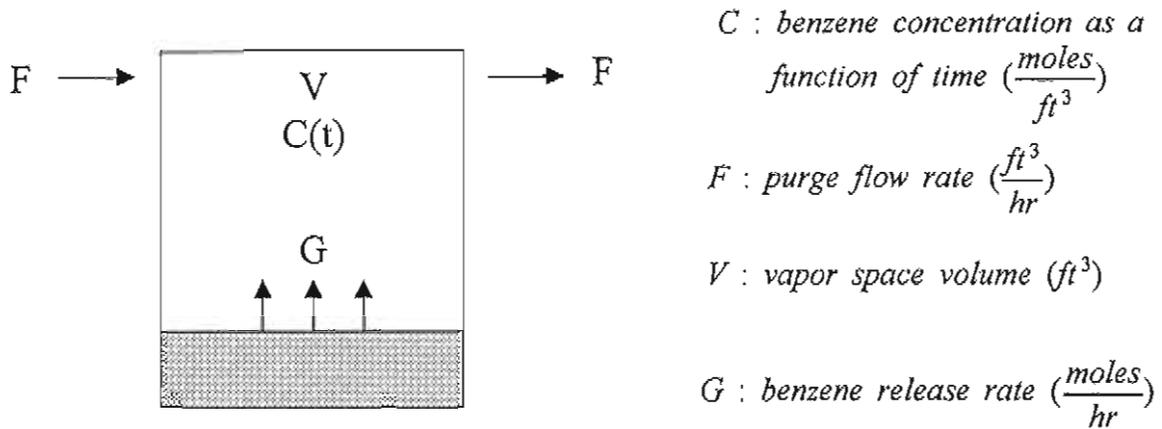
PURPOSE: To calculate the time required for benzene to reach a flammable concentration (assuming enough oxygen is available to sustain combustion).

ASSUMPTIONS:

- The initial benzene concentration at time t = 0 is zero.

- The benzene mass transfer rate from the liquid phase to the vapor phase, denoted by G, is constant.

- The vapor space of the tank is assumed to be well mixed.

- Conditions are calculated under a temperature of 25° C and a pressure of 1 atmosphere.

- Only benzene contributes to the CLFL.

DATA: liquid slurry volume = 200,000 gallons

$$F = 300 \ \frac{ft^3}{min} \ (60 \ \frac{min}{hr}) = 18,000 \ \frac{ft^3}{hr}$$

$$V = 1.1 \times 10^6 \ gal(.1337 \ \frac{ft^3}{gal}) = 147,000 \ ft^3$$

Note that the vapor space volume is calculated by subtracting the slurry volume (2.00 x 10^5 gal) from the total tank volume (1.3 x 10^6 gal).

RESULTS: For large benzene release rates, a flammable mixture (assuming MOC) can develop very rapidly; for a release rate of 1.0 x 10^6 µg/liter-hr, the CLFL would be reached in 5 minutes. For smaller release rates, between 10,380 and 1.0 x 10^6 µg/liter-hr, this time would be longer, but flammability could still be reached. Release rates as low as 10,380 µg/liter-hr can result in the eventual development of a flammable mixture.

Section 4 of this report presents a graph of the time to reach CLFL versus the benzene release rate for ventilation flow rates of 300 scfm (design basis minimum) and 750 scfm (normal flow rate). This graph shows that (1) the impact of the purge flow rate is inconsequential for benzene release rates of 100,000 µg/liter-hr and higher, as the purge system is rapidly overwhelmed for these high release rates; (2) the impact of the purge flow rate is significant for lower release rates; and (3) a higher purge flow rate allows for higher benzene release rates without the development of a flammable mixture.

CALCULATIONS: The mass transfer differential equation and solution are as follows:

$$V\frac{dC}{dt} = G - FC \tag{1}$$

$$C(t) = \frac{G}{F}\left[1 - e^{-\alpha t}\right] \quad where \ \alpha = \frac{F}{V} \tag{2}$$

The postulated generation rate of benzene resulting from the decomposition of benzene has varied between 12,000 and 9.1 x 10^6 µg/liter-hr. This calculation uses a value of 1.0 x 10^6 µg/liter-hr to calculate G.

$$G = 1.0 \times 10^6 \frac{\mu g}{liter-hr}\left[(200,000gal) \ (3.785\frac{liter}{gal})\right]\left[(1\times10^{-6}\frac{g}{\mu g})(\frac{1 \ mole}{78 \ g \ benzene})\right] \tag{3}$$

$$G = 9705 \ \frac{moles}{hr} \ of \ benzene$$

The time constant is calculated as follows:

$$\alpha = \frac{F}{V} = \frac{(18,000 \ \frac{ft^3}{hr})}{(147,000 \ ft^3)} = 0.122 \ hr^{-1} \tag{4}$$

The benzene concentration consistent with the CLFL is 13,500 ppm. The value of C consistent with CLFL is the following:

$$C = (13,500\ ppm)\left(\frac{10^{-6}\ g\ C_6H_6}{g\ N_2 \cdot ppm}\right)\left(\frac{mole\ C_6H_6}{78\ g\ C_6H_6}\right)\left(\frac{28\ g\ N_2}{mole\ N_2}\right)\left(\frac{28.32\ liters}{ft^3}\right)\left(\frac{mole\ N_2}{24.45\ liters}\right) \quad (5)$$

(Note: 24.45 liters/mole reflects the tank temperature of 25° C.)

$$C = 0.0056\ \frac{moles\ C_6H_6}{ft^3}$$

Thus, the time required to reach the CLFL can be determined by solving equation (2) for 0.0056 moles of benzene per cubic foot.

$$t = -\frac{1}{\alpha}\ln\left(1 - \frac{CF}{G}\right) = \frac{-1}{0.122hr^{-1}}\ln\left[1 - \frac{\left(0.0056\ \frac{moles}{ft^3}\right)\left(18,000\ \frac{ft^3}{hr}\right)}{\left(9705\ \frac{moles}{hr}\right)}\right] \quad (6)$$

$$t = 0.085\ hr\ or\ approximately\ 5\ min$$

Another key value is that benzene release rate which would lead to the buildup of a flammable mixture in steady state (i.e., t→ ∞). For the same slurry volume (200,000 gal) and flow rate (300 scfm):

$$G_{t=\infty} = C(t=\infty) \cdot F = \left(0.0056\ \frac{moles}{ft^3}\right)\left(18,000\ \frac{ft^3}{hr}\right)$$

$$G_{t=\infty} = 100.8\ \frac{moles}{hr} \quad (7)$$

This is equivalent to a normalized benzene production rate of 31,700 μg/liter-hr.

For a flow rate of 750 scfm:

$$G_{t=\infty} = 252\ \frac{moles}{hr}$$

This is equivalent to a normalized benzine production rate of 10,380 μg/liter-hr.

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GLOSSARY

µg	microgram(s)
CLFL	composite lower flammability limit
CsTPB	cesium tetraphenylborate
DOE	Department of Energy
eV	electron volt(s)
g	gram(s)
HLW	high-level waste
HPLC	high-pressure liquid chromatograph
JCO	Justification for Continued Operation
kg	kilogram(s)
KTPB	potassium tetraphenylborate
LCO	Limiting Condition of Operation
LLW	low-level waste
MOC	minimum oxygen for combustion
MST	monosodium titanate
Na_2S	sodium sulfide
NaTPB	sodium tetraphenylborate
nCi/ml	nanocuries per milliliter
NMR	nuclear magnetic resanance
PBA	phenylboronic acid
PNNL	Pacific Northwest National Laboratories
ppm	parts per million
rem	Roentgen equivalent man
scfm	standard cubic feet per minute
SRS	Savannah River Site
TPB	tetraphenylborate