97-0000270

Department of Energy
Savannah River Operations Office
P.O. Box A
Aiken, South Carolina 29802

JAN 28 1997

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DNF SAFETY BOARD

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

Dear Mr. Chairman:

SUBJECT: Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 96-1, Test Plan Deliverables for January 1997

The enclosed test program document provides the test plan deliverables scheduled for January 1997 as defined in the Implementation Plan for DNFSB Recommendation 96-1. These test plan deliverables include:

- Test Plan for Stability of Solid Cesium and Potassium Tetraphenylborate
  (Commitment # 3, Milestone # 5.2.2-2)
  This test plan describes the test activities necessary to determine whether direct chemical decomposition of solid Cesium and Potassium Tetraphenylborate (TPB) are a major mechanism for generating benzene in the In-Tank Precipitation (ITP) process.
- Test Plan for Benzene Retention Mechanisms and Capacities
  (Commitment # 5, Milestones # 5.2.3-1 & # 5.2.3-2)
  This test plan describes the test activities necessary to determine the capacity and distribution of benzene in Potassium TPB slurries above the apparent solubility limit, determine how the benzene is retained, and determine the relative releasability of the different retention mechanisms.
- Test Plan for Laboratory Benzene Release Studies
  (Commitment # 5, Milestone # 5.2.4-1)
  This test plan describes the test activities necessary to determine the apparent solubility and the slurry-vapor equilibrium relationships for Potassium TPB slurries.

This test program document describes the overall ITP process chemistry testing program for resolution of Recommendation 96-1 and provides overview sections common to all program components. Test Plans describing the specific testing activities to be conducted are included as Appendices A through E. Please note that Appendix A is the Test Plan for Catalytic Decomposition of Soluble Tetraphenylborate which was issued to you by letter on December 20, 1996. Also, Appendix E is reserved for the Test Plan for Real Waste Material Tests which is scheduled for delivery in April 1997.

The US Department of Energy, Savannah River Operations Office, has completed the actions necessary for Recommendation 96-1 milestone deliverables # 5.2.2-2, 5.2.3-1, 5.2.3-2, & 5.2.4-1, and proposes their closure. Copies of these deliverables have been provided and discussed with your staff.

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

Sincerely,

A. Lee Watkins

A. Lee Watkins
Assistant Manager
for High Level Waste

ED:JWM:kl

PC-97-0027

Enclosure:
Test Program for Resolution of
DNFSB Recommendation 96-1

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TEST PROGRAM FOR RESOLUTION OF DNFSB RECOMMENDATION 96-1 (U)

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1.0 EXECUTIVE SUMMARY

On August 14, 1996, the Department of Energy (hereafter referred to as the Department) received Recommendation 96-1 from the Defense Nuclear Facilities Safety Board (hereafter referred to as the DNFSB). The recommendation addresses safety concerns at the In-Tank Precipitation (ITP) facility at the Savannah River Site near Aiken, SC.

Safety issues of concern to the DNFSB involve the level of understanding of tetraphenylborate (TPB) chemistry regarding TPB decomposition resulting in benzene generation, retention and release, and, based on this level of understanding, the adequacy of existing safety measures. Issue resolution includes:

- identification of important decomposition catalysts that will be encountered in ITP with a quantitative understanding of their effects;
- establishment of the chemical and physical mechanisms that determine how and to what extent benzene is retained in the waste slurry;
- understanding of the extent of the benzene release during mixing pump operation or other mechanisms leading to rapid release of benzene;
- improved understanding of the mechanisms leading to high benzene generation and release observed in Tank 48 in November and December, 1995, and March 1996;
- improved understanding of the rapid increase in measured soluble cesium which occurred following reprecipitation with sodium tetraphenyborate in experiments in mid-1996; and,
- affirmation of or modification to ongoing improvements to the facility design.

The Board recommended that in-plant testing involving significant quantities of TPB or new waste additions to ITP be deferred until a better understanding of TPB chemistry is achieved and the adequacy of safety measures has been affirmed. This recommendation was made at a time when the authorization basis for safe operation of the ITP facility was transitioning from fuel control to oxygen control. Some modifications to the ITP nitrogen inerting systems were in progress at that time and will continue at risk while a revised authorization basis is developed. Results of the chemistry program will serve as inputs to the authorization basis including a comprehensive defense-in-depth safety strategy, and development of controls and engineered systems for the prevention or mitigation of a potential tank deflagration.

The principle underlying cause of benzene generation is believed to be catalytic decomposition of soluble TPB. Catalysts are believed to be copper ion, metal hydroxides and possibly organics commonly present in Savannah River Site waste. Benzene generation is also influenced by other factors that will be considered in the research including such parameters as temperature, solids concentration and hydroxide concentration. A significant amount of the benzene generated is retained prior to release. Likely retention mechanisms are emulsions/rag layers, free layers and adsorption on solids; however, additional study is necessary to confirm these mechanisms. The primary release mechanism appears to be operation of the mixing pumps; however, not all important benzene generation and release mechanisms are quantified or known. Additional research and testing is required.

Safety issue resolution consists of four integrated programs:

- A combination of preventive and mitigative controls and engineered systems to prevent and/or mitigate benzene deflagration will be developed in parallel with investigation of the following three chemistry issues, and will be reviewed and finalized once a better understanding chemistry issues has been developed,

- The scientific understanding of the reactions leading to the generation of benzene in the ITP Facility will be improved to ensure that measures to prevent and/or mitigate deflagration are adequate,
- The scientific understanding of the mechanisms leading to the retention of benzene in the ITP System will be improved to ensure that measures to prevent and/or mitigate deflagration are adequate, and
- The scientific understanding of mechanisms involved with the release of benzene in the ITP System will be improved to ensure that measures to prevent and/or mitigate deflagration are adequate.

These programs have been described by the Implementation Plan for Resolution of Recommendation 96-1 (reference 1), which requires the development of six Test Plans further describing programs related to benzene generation, retention and release. This Test Program document, its appendices and revisions satisfy these deliverables. The Test Program document provides background on the High Level Waste System and flowsheets, a description of the In-Tank Precipitation Process and descriptions of key process interfaces. The overall chemistry testing program for resolution of Recommendation 96-1 is described and overview sections common to all program components are included. Test Plans specific to each deliverable objective are attached as appendices. Two of the six test plans related to benzene retention mechanisms and capacity are combined into a single document, which is provided as Appendix D. The individual Test Plans should be read in the context of the Test Program document to understand how the different elements of the testing fit together to resolve the issues.

2.0 BACKGROUND

2.1 HIGH LEVEL WASTE COMPLEX OVERVIEW

The Savannah River Site (SRS) near Aiken, SC, has begun the task of vitrifying high level radioactive waste into a durable borosilicate glass. In over 30 years of operation, about 72 million gallons of high level radioactive waste have been generated at the Savannah River Site. This waste has subsequently been evaporated to 28 million gallons and stored in large underground tanks, and is now being pretreated, melted into glass and poured into stainless steel canisters for eventual disposal in a geologic repository.

The evaporation process has resulted in the waste being separated into a water soluble salt solution and saltcake, and an insoluble sludge of metal hydroxides and oxides. The majority of the high level radioactive waste volume is stored in waste tanks as salt cake. Water is added to the salt cake and the resulting salt solution is transferred to the In-Tank Precipitation (ITP) Facility. In the ITP process, salt solution is decontaminated for disposal as low-level radioactive waste by the addition of sodium tetraphenylborate to precipitate the soluble salts of potassium and cesium and the addition of sodium titanate to adsorb residual strontium, plutonium, and other actinides. The resulting slurry is filtered and the decontaminated filtrate is blended in the Saltstone Facility with cement, slag and flyash for disposal as a low-level radioactive waste.

The concentrated precipitate is processed in the DWPF Late Wash Facility (LWF) to remove the corrosion inhibitor sodium nitrite prior to processing in the Salt Processing Cell where most of the organic material is removed. The tetraphenylborate compounds contained in the precipitate react in the presence of formic acid and copper (II) catalyst. The products of this reaction are aromatic organic compounds (benzene, phenol, and minor amounts of higher boiling aromatics) and an aqueous phase known as Precipitate Hydrolysis Aqueous (PHA). The PHA contains the cesium, soluble formate salts, boric acid and excess formic acid.

The sludge portion of the waste is washed to remove soluble salts. If necessary, insoluble aluminum is removed through high temperature caustic dissolution. Thus, the radioactive waste from the SRS Tank Farms is pretreated in two forms: precipitate slurry and sludge slurry. The waste is then processed and blended in the Defense Waste Processing Facility (DWPF) before it is vitrified, poured into canisters, sealed and placed in interim storage. Sludge slurry transfers to DWPF began in March 1996.

The sludge is transferred directly into the Sludge Receipt and Adjustment Tank (SRAT) and then neutralized with nitric acid. The PHA is then added to the sludge (at boiling). After the PHA and sludge are blended and processed in the SRAT, this SRAT product is transferred to the Slurry Mix Evaporator where a borosilicate glass frit is added and the slurry is concentrated to produce melter feed.

2.2 IN TANK PRECIPITATION OVERVIEW

The objective of the ITP process is to chemically treat radioactive salt solution such that the bulk of the radionuclides can be separated into a low volume, high activity stream which can be incorporated into borosilicate glass while the remaining fraction is solidified as grout and disposed of as low level waste. Changes in the ITP process can impact other HLW processing facilities such as Late Wash and Saltstone.

In the ITP process, monosodium titanate and sodium tetraphenylborate (NaTPB) are added to salt solution to adsorb Sr-90/Pu-238 and precipitate Cs-137, respectively. The chemical addition and subsequent reaction form a precipitate slurry which is then filtered. The filtrate is a decontaminated salt solution that is stripped of benzene, sampled and then pumped to a separate facility, Saltstone, where it is mixed with cement, slag and flyash to form a grout and disposed of as low level waste. The precipitate remaining after filtration is washed with water to reduce the Na concentration, sampled and transferred to the Defense Waste Processing Facility for nitrite removal washing (Late Wash Facility), combined with radioactive sludge and vitrified (See Figure 1).

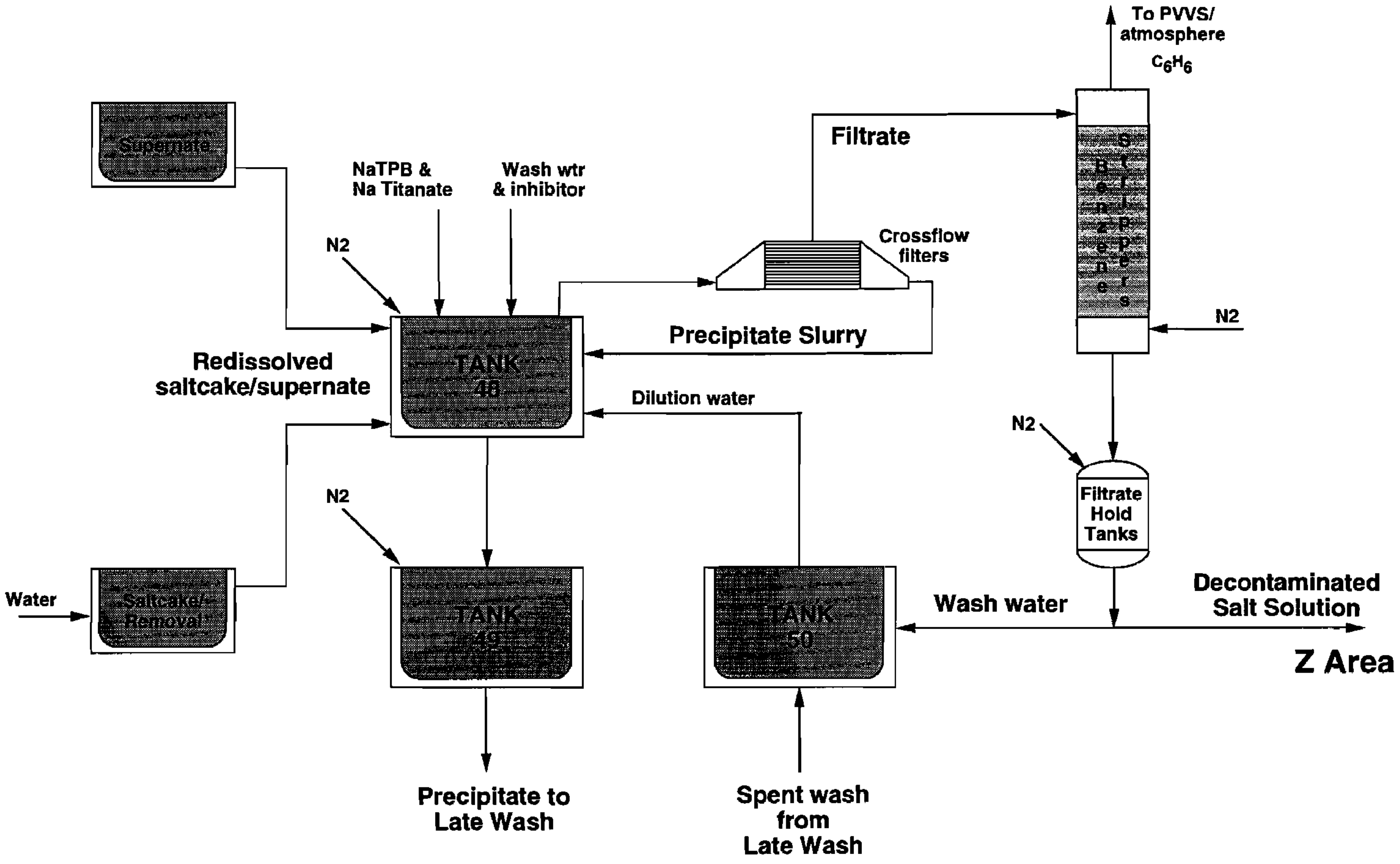
2.3 INITIAL RADIOACTIVE OPERATIONS

The ITP facility initiated radioactive operations in September 1995 with the addition of 130,000 gallons of salt solution and 37,300 gallons of NaTPB to the heel of precipitate in Tank 48 that remained from the 1983 demonstration. Initial operations were conducted under the guidance of the Radioactive Operations Commissioning Test Program (reference 2) which specified controlled evolutions and additional sampling and monitoring requirements. During October, the first of three pump tests was conducted in which the effect of tank mixing was determined. This test was characterized by a nearly constant benzene release from the liquid phase to the vapor phase that maintained the vapor space concentration at nearly 60 ppm during pump operations. Following the completion of the first pump run on October 12, 1995, the tank remained quiescent until October 20, 1995.

Filtration began on October 20, 1995, and continued until October 25 producing 140,000 gallons of filtrate. Filtration was conducted at a nearly constant temperature of 39°C. Filtration was followed by the second pump run starting October 26. The benzene concentration in the vapor space was higher than expected, but well below the Operational Safety Requirement (OSR) limit of 3400 parts per million (ppm). A water addition was made without an increase in benzene concentration. A second filtration step was conducted producing 160,000 gallons of filtrate and bringing the liquid level in Tank 48 to 160,000 gallons. The third pump run, which was designed to be conducted at higher temperatures to support oxygen control testing, resulted in heating the tank to 52°C. Again, the benzene concentration was higher than expected but still below the OSR limit. The tank was quiescent during ventilation tests and had cooled to 30°C by December 1, 1995.

On December 1, 1995, all four slurry pumps were operated for about 3.5 hours to prepare the tank for sampling. Pump operation was then halted due to the observed high benzene readings (2,000 ppm) in the tank vapor space well before the OSR limit was approached. Data from Tank 48 instrumentation and tank sample analyses indicated that NaTPB decomposition had occurred. Efforts began to remove the benzene that had accumulated in the liquid. A Justification for Continued Operation (JCO) was written to incorporate additional fuel controls on the rate of benzene release that would be allowed during pump operation. A series of single pump runs were conducted under the JCO to deplete the benzene from the tank between December 8, 1995, and January 3, 1996. From January 3 to March 5, 1996, the tank was quiescent. During this period, an alternate nitrogen system was installed and the JCO was revised to credit nitrogen inerting and to provide less restrictive pump operating limits.

Figure 1
In-Tank Precipitation



On March 5, 1996, one slurry pump was operated at low (600 rpm) speed. A rapid benzene release rate was seen in the tank as indicated by vapor space concentration of benzene, and pump operation was terminated after 14 minutes. This data indicated periods of non-uniform distribution of benzene in the tank vapor space. Starting on March 8, periodic pump operations were resumed in a conservative, controlled manner in continued efforts to deplete benzene from the tank. Initial operations employed only one slurry pump. As benzene release rates decreased, additional pumps were started. By April 25, 1996, all four pumps were operating at the maximum speed of 1,180 rpm. From November 5, 1995, to April 22, 1996, approximately 8,500 kg of benzene were removed from Tank 48. Since April, 1996, Tank 48 has essentially been depleted of benzene as indicated by the very small releases observed even with operation of all four pumps.

The Department deferred additional waste processing in ITP until such time as an improved understanding of NaTPB chemistry has been achieved and the appropriate modifications to facility hardware, engineered controls and administrative controls have been completed.

3.0 IN TANK PRECIPITATION FLOWSHEET

One of the key baseline assumptions made by the Implementation Plan is that the basic precipitation process will be preserved and that an acceptable authorization basis and operating envelope can be developed using the basic process configuration of the ITP facility. Minor plant configuration changes have been recommended to better accommodate the benzene generation.

3.1 PRECIPITATION AND SORPTION

The first step in the ITP process is a transfer of approximately 500,000 gallons of salt solution (new waste) from a waste tank to Tank 48 (see Figure 1). Approximately 100,000 gallons of dilution water is then added to Tank 48. Approximately 6,000 gallons of sodium titanate is added to Tank 48 to adsorb soluble radioactive strontium and plutonium via ion exchange.

- $Sr^+ + NaTi_2O_5H + OH^- => Sr(NaTi_2O_5) + H_2O$
- $Pu^+ + NaTi_2O_5H + OH^- => Pu(NaTi_2O_5) + H_2O$

Sodium tetraphenylborate is then added to Tank 48 to precipitate the soluble cesium (primarily Cs-137). NaTPB also precipitates potassium and other species in the waste.

- $Cs^+ + NaB(C_6H_5)_4$ ´ $Na^+ + CsB(C_6H_5)_4$
- $K^+ + NaB(C_6H_5)_4$ ´ $Na^+ + KB(C_6H_5)_4$

Originally some 36,000 to 40,000 gallons of NaTPB solution was to be added to each batch. This quantity was based on the stoichiometric amount required to precipitate both the cesium and potassium plus about 30% excess to ensure the precipitation reaction occurred rapidly and to ensure sufficient NaTPB remained during the washing step to meet the filtrate decontamination requirements. This excess amount of NaTPB exceeds the solubility limit for NaTPB in Tank 48; therefore NaTPB exists in both soluble and solid form.

NaTPB, KTPB, and CsTPB are all subject to potential decomposition reactions which result in the production of benzene. Decomposition can be caused by radiolysis or thermal breakdown (catalyzed by copper and potentially other soluble or insoluble metal species or organics). This benzene is then accumulated in Tank 48 by dissolution in the salt solution, adsorption by the TPB solids, and by other means. Benzene is released via evaporation, which is enhanced by pump operation. The accumulation of benzene vapors in the tank poses a potential deflagration hazard. The parameters affecting benzene generation, retention and release need to be better understood to assure adequate engineering and administrative features exist to protect the tanks from deflagration.

This potential hazard is present wherever NaTPB and its decomposition products (including benzene) are processed, including Late Wash and Saltstone.

3.2 CONCENTRATION

The next step concentrates the radioactive waste by filtration. The volume in Tank 48 is reduced to about 154,000 gallons, or that volume which is sufficient to concentrate the solids to about 10 wt%. Filter feed pumps force the low-activity salt solution (filtrate) through a filter and then to one of two benzene strippers. The precipitate is returned to Tank 48.

Radiation detectors are located on the filtrate line exiting the filter. High radiation indicates a release of highly radioactive material from the filter into the filtrate piping. Actuation of a high radiation alarm causes the downstream isolation valves to close.

During filtration (concentration and washing), slurry pumps are used to mix the contents of Tank 48. Slurry pumps draw liquid waste through the bottom of the pump volute and discharge it through nozzles on the side of the volute. Slurry pumps are variable speed.

Both the degree of mixing and the rate of tank temperature rise can be controlled by the pump speed. A closed loop cooling water system circulates cooling water through carbon steel coils in Tanks 48, 49 and 50. When four slurry pumps are operated at full speed (1180 rpm) at a tank volume of 150,000 gallons with cooling water on, the tank temperature will increase about 1°C per day. Under the same conditions at low pump speed (600 rpm) no tank temperature increase has been detected. When four pumps are operated at 1180 rpm with cooling water turned off, the maximum measured temperature rise is 3°C per day (reference 3).

During concentration it is not necessary to have "complete" mixing since the objective is to remove the liquid fraction and the filter is more efficient with lower solids-containing precipitate. Therefore, the mixer pumps can be operated at low speed and avoid tank heat up during concentration. The tank contents are also heated by radionuclide decay, but the effect is negligible compared to the effect of mixer pumps (reference 3).

The filtrate produced (decontaminated salt solution) is stripped of residual benzene prior to being transferred to Saltstone. Decontaminated salt solution (DSS) and wash water (see below) contain the same soluble species as Tank 48 including NaTPB and benzene. It has recently been determined that Tank 22 (the original wash water storage tank) is not suitable for this service. Therefore, Tank 22 will be removed from the ITP Facility flowsheet and Tank 50 will be substituted as a wash water storage tank. DSS will be sent directly to Saltstone. A new DSS storage tank is being considered to improve production capability.

Two to four additional precipitation and concentration cycles are then processed in subsequent batches to increase the amount of precipitate available for washing. The batch size and number of batches vary depending upon the new waste cesium and potassium concentrations and upon any volumetric limits imposed upon Tank 48.

3.3 WASHING

Upon completion of the concentration phase, the precipitate remaining in Tank 48 is washed to reduce the sodium and nitrate content of the precipitate remaining in the tank. The precipitate is filtered in a cycle similar to the concentration cycle. Wash water is added to Tank 48 at the same rate that spent wash water is being removed by the filtering process. Wash water is well water that has been treated with the corrosion inhibitor, sodium hydroxide. Washing continues until the soluble sodium concentration is approximately 0.2 molar sodium.

As described above, wash water also has the same soluble components (although reduced concentration) as Tank 48. Tank 50 will be placed into wash water storage service. The stored wash water will be recycled to Tank 48 for use as dilution water during subsequent batches.

As with concentration it is not necessary to have "complete" mixing during the wash step. The objective is not really solids washing (via wash water/solids contact); instead it is soluble component dilution. The tank needs to be mixed sufficiently to ensure that the wash water is mixed with the salt solution. Mixer pump operation at low speed to avoid tank heat up is adequate.

3.4 BENZENE STRIPPING

The benzene stripper columns remove benzene from the filtrate or wash water stream. Benzene Stripper Column 1 is used during the concentration cycle; Benzene Stripper Column 2 is used for the wash cycle. The two stripper columns have different capacities based on flow rate differences between the concentration step and the washing step. The stripped filtrate is pumped to one of two filtrate hold tanks.

The filtrate is stored in the filtrate hold tank while being sampled. If the sample analysis is within specification, the filtrate is pumped to Z Area. If the sample analysis is unsatisfactory (e.g., contains unacceptable levels of benzene), the filtrate is gravity drained back to Tank 48 for reprocessing.

Tributyl phosphate is added as an anti-foam agent to the filtrate in the ITP process system. Excessive foaming hampers benzene removal in the benzene stripper columns.

3.5 FILTER CLEANING

Following each concentration and wash evolution, the Precipitate/Filtrate System is chemically cleaned. This cleaning consists of flushing the process piping with inhibited water, followed by additions of oxalic acid and/or caustic (NaOH). The piping is again flushed with inhibited water to remove any remaining acid or caustic.

The addition of oxalic acid is known to start decomposition of TPB. The return to Tank 48 of the spent oxalic acid solution (200 - 250 gallons following three soak periods) has the potential to start decomposition. The cleaning solution is returned to Tank 48 with the mixing pumps operating to ensure rapid neutralization (the neutralization reaction rate significantly greater than the decomposition reaction rate). Calculations have been completed which indicate tank mixing is adequate to ensure rapid neutralization (reference 4).

Process Verification Test 1 (PVT-1) included a full scale filter cleaning operation as described above. The report on the test data is deliverable 5.2.2-3 of the Implementation Plan.

3.6 PRECIPITATE STORAGE

The resulting washed precipitate in Tank 48 is transferred to Tank 49, using a single-speed transfer pump through a dedicated transfer line. The precipitate is stored in Tank 49 until transferred to the Late Wash Facility, to an S Area storage tank located in the Low Point Pump Pit, and then on to DWPF.

During storage, sodium nitrite ($NaNO_2$) is added as a corrosion control chemical. However, sodium nitrite alters the acid hydrolysis reactions in the DWPF Salt Processing Cell. For this reason the sodium nitrite must be washed out prior to processing. This washing is conducted in the DWPF Late Wash Facility (LWF).

Also during storage, benzene continues to be produced from both radiolysis and NaTPB decomposition. As with Tank 48, the benzene retention and release is a function of several parameters which need to be further understood.

Tank 49 is equipped with mixer pumps similar to those in Tank 48 which are used to ensure adequate mixing during transfers to DWPF or to increase the benzene release rate.

3.7 LATE WASH FACILITY

The LWF is similar in function and operation to the ITP Facility. The precipitate is received into a 6500 gallon stainless steel tank where it is agitated until washing begins. The facility has the capability to add NaTPB to precipitate any soluble cesium prior to washing and to add NaTPB to the wash water to ensure the presence of sufficient TPB during the washing step. Direct NaTPB addition is not anticipated.

The precipitate is recirculated through the filter and back to the Precipitate Hold Tank using an 1100 gpm low shear pump. The filter is identical to the ITP facility filter. Filtrate is collected in the 6500 gallon tank and held until transfer to Tank 50 via a dedicated underground line to Tank 50. (As with ITP filtrate, Tank 22 was originally planned).

Unlike ITP no mixer pumps are required; the precipitate filter feed pump and agitator ensure the tank is adequately mixed during washing.

The LWF has potential for benzene generation, retention and release as well. The ITP chemistry program has been expanded to include a range of testing to satisfy the needs of the LWF to ensure its safe operation.

3.8 SALTSTONE

Decontaminated salt solution is received into the 40,000 gallon Salt Solution Hold Tank (SSHT) at Saltstone where it is held until it is mixed with flyash, slag and cement. The Saltstone mixture is pumped into a concrete vault where the Saltstone is allowed to cure.

Since the DSS contains the same soluble species as Tank 48 including soluble NaTPB, the Saltstone Facility must also contend with the potential for benzene generation and accumulation. The ITP chemistry program has been expanded to include a range of testing for DSS in Saltstone.

4.0 FLOWSHEET CHANGE SUMMARY

For the reasons provided above, the following HLW complex flowsheet changes have been accepted.

- Tank 22 has been removed from the flowsheet and will not receive spent wash water.
- Tank 50 will be converted to spent wash water storage for both ITP and LWF.
- LWF wash water will be rerouted to avoid the possibility of inadvertent transfers to other parts of the tank farm by the addition of a dedicated underground transfer line to Tank 50.
- DSS will be pumped directly from the ITP Filtrate Hold Tank to the Saltstone SSHT. (A new DSS storage tank is being considered for production improvement.) A new valve box will be required to allow the Filtrate Hold Tank transfer pumps to go either to Saltstone or Tank 50.

5.0 PROCESS CHEMISTRY CHANGES

The following actions will be taken to maintain the benzene generation, retention and release as low as possible for each part of the High Level Waste complex:

- The excess (above stoichiometric) NaTPB added during the precipitation step will be limited to less than that which is soluble (about 17% of stoichiometric excess at 5.0 M Na salt concentration). Based on the current understanding, this amount of excess is sufficient to ensure the DSS is less than 35 nCi/g.

- Since the stoichiometric amount of NaTPB depends upon the amount of Cs and K in the fresh waste, and the K has a high analytical uncertainty, the NaTPB will be added in batches. By adding less than the stoichiometric amount and sampling for soluble Cs, the addition amount can be more accurately determined. The target total addition will be the stoichiometric equivalent plus the amount required to maintain an excess of soluble NaTPB without producing solid NaTPB. This should result in a soluble Cs concentration < 35 nCi/g.

- The temperature in all tanks containing TPB species (or decomposition products) will be limited to a specified value. This value will be based on the kinetic information obtained from the chemistry program. The temperature limit is expected to be in the range of 35 to 45°C.

- This temperature limit combined with the molar excess NaTPB is expected to maintain the soluble Cs concentration less than 35 nCi/g for up to one month, providing adequate time to complete filtration. The wash water soluble Cs concentration must be maintained < 10,000 nCi/g, based on the shielding limit for the filter building. If process times lengthen such that the soluble Cs exceeds these limits additional NaTPB will be added to reprecipitate the Cs.

- Target additions of NaTPB for reprecipitation will be based on the stoichiometric amounts plus the molar concentration excess required to maintain the total mass of TPB solids in equilibrium such that the resulting soluble Cs is again less than the limit.

6.0 KEY PROCESS INTERFACES

Using the operating strategy described above, there are several key operational interfaces between the HLW complex facilities. Interfaces between ITP and other HLW complex tank farm diversion boxes and pump pits are being eliminated except for waste transfers to ITP. The key remaining interfaces are described below:

6.1 SALTSTONE

During DSS production, ITP and Saltstone will be close coupled (ITP filtrate hold tank will be pumped directly to the Saltstone salt solution hold tank). The ALARA guidelines for current Saltstone shielding is 35 nCi/g, therefore the DSS must contain < 35 nCi/g. (In the past this limit was 85 nCi/g based on the DSS blending with other waste which occurred in Tank 50. This blending no longer exists.)

The DSS will contain the same soluble compound concentrations as Tank 48, including the soluble NaTPB, NaTPB decomposition products and benzene. Benzene will be reduced to less than 5 ppm for wash water and 2 ppm for DSS (per process requirements) using the stripper column.

The chemistry program described below includes the necessary range of testing to gain an adequate understanding of benzene generation, retention and release for DSS. As with Tank 48, appropriate controls will be placed on the potential fuel (NaTPB, decomposition products, and benzene) and processing temperature to ensure safe storage and handling of DSS at Saltstone.

6.2 LATE WASH

Late Wash will receive the concentrated precipitate which has been stored in Tank 49. Based on the amount of NaTPB added in Tank 48, process history (i.e., amount of washing) processing temperature, and processing time in Tank 48 and 49, some NaTPB, decomposition products and benzene will be present in Tank 49. The chemistry program is anticipated to validate the position that benzene can be safely depleted from Tank 49 using the mixer pumps. Any remaining potential fuel source will be transferred to Late Wash.

The chemistry program described below includes the necessary range of testing to gain an adequate understanding of benzene generation, retention, and release under Late Wash process conditions.

6.3 LOW POINT PUMP PIT

The Late Wash precipitate product will be transferred to the low point pump pit precipitate tank for storage prior to transfer to the Salt Processing Cell in DWPF. The range of testing for Late Wash encompasses conditions in the low point pump pit precipitate tank.

Based on the Hazards Analysis currently being completed for the facilities, and on validation by the chemistry program, some modifications to ensure safe processing may be required for these facilities.

7.0 CHEMISTRY PROGRAM FOR RESOLUTION OF THE ITP BENZENE ISSUE

As described above, the chemistry program for resolution of the benzene issue at the ITP facility has been expanded to include other affected HLW complex facilities. However, attempts have been made to the maximum extent reasonable to contain the problem within ITP. The chemistry program is based on the configuration described above. The chemistry program systematically evaluates the mechanisms and conditions that may lead to benzene generation, retention and release. The dominant mechanisms for each step will be identified and synergistic interactions evaluated to determine bounding conditions. Experiments have been designed to challenge existing hypotheses and uncover weaknesses. The experimental results will be confirmed with radioactive waste tests. The improved understanding of benzene chemistry and behavior resulting from these tests will be used to provide the comprehensive safety strategy needed for HLW complex operations.

The underlying philosophy described in the Implementation Plan is one of parallel activities supporting the ultimate goal of achieving facility restart in a safe and timely manner. Some tasks will be initiated based on existing data and bounding assumptions, while the work being done to confirm the assumptions proceeds in parallel. This approach entails some programmatic risk (i.e., cost and schedule) should the assumptions be proven wrong; however, it does not entail any safety risk.

Initial material balances have been completed to provide bounding values for the key parameters affecting benzene generation, retention and release, based on current understanding. These bounding values will be used in the development of the revised authorization basis and to drive the modification of equipment, facilities, procedures and controls necessary to support safe operation. The initial results have also been used to define further activities which will refine the bounding values for benzene generation, retention and release.

The chemistry program will be performed in parallel with the authorization basis modifications. As information is obtained, it will be evaluated with respect to the authorization basis development task to ensure that:

- the actual values of the safety analysis parameters are truly bounded by the assumed values, and
- over-conservatism in the assumed values is removed as early as possible.

The result of this approach will be finalization of the authorization basis and all associated modifications to equipment and implementation of other controls soon after completion of the studies and experiments.

There is a small programmatic risk that chemisty results obtained late in the process will indicate that the employed values are not truly bounding. The potential time savings associated with the parallel approach justifies accepting this risk. In the unlikely event that the assumptions are shown to be non-conservative, additional work will be performed to ensure that the authorization basis and facility design reflect the acceptable values prior to resuming operations.

7.1 GENERAL APPROACH

The thrust of this program is to determine the overall generation rate of benzene and understand the parameters which affect benzene retention and release. This information is then used to conservatively define the engineered features, operating limits and administrative controls necessary to prevent and/or mitigate deflagration. These engineered features, operating limits and administrative controls will then be incorporated in the authorization basis for ITP, and other HLW complex facilities as necessary.

The chemistry program consists of a series of tests using simulated waste to determine the generation, retention and release mechanisms while varying key parameters such as catalyst concentration and temperature to include bounding conditions. The experiments incorporate both statistical and single variable designs. The bounding tests will then be confirmed with radioactive waste. These confirmed bounding generation rates will be used in conjunction with the slurry physical properties and ITP mass transfer coefficients to determine a bounding release rate from the slurry to the vapor phase. This release rate will then be used to confirm the adequacy of existing systems and in developing design bases for new engineered features or administrative controls, as necessary. The planning and results of the chemistry test program will continue to be reviewed with external experts in several technical areas including organic chemistry, catalysis, mass transfer, safety, tank mixing, and other areas as appropriate.

The chemistry tasks must accomplish the following objectives:

Benzene Generation: Knowledge of the benzene generation rate, when combined with the bounding liquid retention capacity, is essential for determining the time between pump runs to achieve adequate benzene depletion. This knowledge is also needed to define process operating parameters to reduce the potential for benzene generation. This information is necessary to support future OSR controls for operating in air-based ventilation (major maintenance), for normal operation, and when the tanks are not processing. To arrive at this position, sufficient information to bound the benzene generation rate from radiolytic, thermal, and chemical breakdown of NaTPB and its intermediates is required. From a safety perspective, this information may be limited to assurance of acceptable rates at some threshold temperature, some bounding radionuclide concentration, and some bounding, known catalyst (provided the administrative controls are in place to verify subsequent batches do not contain an unknown, more active catalyst). Appropriate characterization will be performed using the actual radioactive waste feedstock, including the residual waste in Tank 48, for each batch to be processed in ITP. The potential impact of temperature and other significant variables on TPB solids decomposition must also be known.

Benzene Retention: The retention mechanism(s) must be adequately understood to determine those operations, conditions, and events which can lead to planned and/or inadvertent benzene release. The retention capacity and rate of benzene accumulation in precipitate slurries must be understood to define the inventory of benzene available for release during worst case operating conditions (permitted time in air-based ventilation mode). To arrive at this position, sufficient knowledge of the liquid benzene retention mechanisms at bounding liquid/solids concentrations and validation of the mechanisms for controlled release/depletion of the retained benzne must be achieved. Improved knowledge of benzene retention mechanisms will support and focus the effort to establish release controls.

Benzene Release: Knowledge of the release rate of benzene vapor is necessary to define time of operation and speed of slurry pumps to safely deplete the precipitate of benzene, to determine the impact of liquid additions on vapor concentration, and to bound the maximum possible release from a seismic event during air-based maintenance mode. To arrive at this position, sufficient information must be obtained to bound the benzene release rate from bounding liquid/solids concentrations, from pump operations, from worst case releases from a liquid benzene layer, and due to seismic vibration. This information is to include the effect of temperature and liquid/chemical additions on the release rate.

The overall program for benzene generation, retention and release is described below. Additional details about each program segment can be found in Appendices A to E..

7.2 BENZENE GENERATION

7.2.1 Issue Statement

The current scientific understanding of the reactions leading to the generation of benzene must be improved to ensure that measures to prevent deflagration are adequate.

7.2.2 Resolution Approach

The precipitation of Cs-137 uses an excess of sodium tetraphenylborate. Excess NaTPB will be limited such that no solid NaTPB is present while the KTPB and CsTPB are largely present as solids (precipitate). Soluble TPB species, and possibly solid TPB species, will undergo decomposition.

Research to date has investigated several potential decomposition mechanisms including radiolysis, thermal breakdown, mechanical destruction, acidic reactions and catalysis. As described in the Implementation Plan (reference 1), radiolysis, thermal breakdown, and mechanical destruction have been investigated and are adequately understood. It has been postulated that benzene molecules may be trapped in the solid NaTPB crystal lattice. The "new" flowsheet reduces the trapped benzene hazard by eliminating the solid NaTPB.

Acidic Reactions

The addition of acid(s) is known to result in the destruction of TPB (reference 5). The cross-flow filter in ITP will be cleaned periodically via three separate soaks with 200-250 gallons of 2 wt% oxalic acid per soak. Cleaning solution is returned to Tank 48 with the mixing pumps operating to ensure rapid neutralization with the existing hydroxide in Tank 48 before initiating TPB decomposition (decomposition is much slower than the neutralization reaction). Calculations have been completed which indicate tank mixing is adequate to ensure rapid neutralization. PVT-1 included a full scale filter cleaning operation. Data will be obtained to determine the effect of the addition on benzene generation. This data will be reviewed to determine if additional laboratory or plant data is required.

Catalytic Decomposition

Catalytic decomposition of soluble and potentially solid TPB species has not been as thoroughly researched as the other decomposition mechanisms. Therefore, catalytic mechanisms will be a key focus of the chemistry program.

In TPB chemistry, synergism could exist between two factors described above, e.g., effects of radiation and temperature on TPB reaction rates. If synergistic effects are indicated by the statistically designed experiments with simulants, then further testing of the key variables involved may be required to fully quantify the effects. However, specific tests in this area cannot be prescribed until the interim results of testing on catalytic decomposition of soluble TPB have been evaluated. Issue resolution is focused in two areas: soluble TPB decomposition and solid TPB decomposition.

7.2.3 Soluble TPB Decomposition

Discussion related to soluble TPB decomposition is broken into two segments: minimizing NaTPB usage (to minimize potential benzene generation) and understanding decomposition pathways and rates of reactions. An understanding of the pathways and reaction rates requires the identification of catalysts for TPB decomposition and measurement of reaction kinetics. The details regarding the test plan for catalytic decomposition of soluble TPB are found in Appendix A.

7.2.3.1 Minimum NaTPB

The decontamination requirement for removal of soluble cesium is < 35 nCi/gm. This requirement is achieved by the extremely low solubility of cesium tetraphenylborate in high ionic strength solution and in the presence of soluble TPB. To achieve the high decontamination factor, excess NaTPB is added to the solution to force the cesium out of solution and to improve the precipitation reaction rate. The "excess" of TPB concentration causes cesium to precipitate and establishes equilibrium to the right side of equation 1. To decrease the concentration of NaTPB while maintaining the cesium decontamination factor requires an accurate description of the factors influencing the solubility of cesium tetraphenylborate (CsTPB) and potassium tetraphenylborate (KTPB) as well as the rate of the precipitation reaction. Previous equations used to calculate the CsTPB and NaTPB solubility(reference 6) were based on work by E. Siska (reference 7). These equations were not consistent with observations during testing and demonstration of the ITP process. Further testing is underway to determine the equations that more accurately predict the solubility of CsTPB and KTPB.

$$Cs^{+}_{(AQ)} + TPB^{-}_{(AQ)} \text{<---}K_1\text{--->} CsTPB_{(solid)} \qquad \textit{Equation 1}$$

The equilibrium solubility product constant of CsTPB can be described by equation 2.

$$K_{sp(Cs)} = [Cs^{+}]\,[TPB^{-}] \times (g_{Cs}) \times (g_{TPB}) \qquad \textit{Equation 2}$$

Where $[Cs^{+}]$ and $[TPB^{-}]$ are the molar concentrations of the aqueous species and g_{Cs} and g_{TPB} are the activity coefficients. The activity coefficients are described by the Debye-Huckel equation (reference 8) for dilute solutions, but must be adjusted for the ionic strength for more concentrated solutions (>0.01 m).

Work will be conducted in parallel with the solubility studies to determine the gross effect of NaTPB concentration on the rate of the precipitation reaction. For processing efficiency the precipitation reaction should occur within 24 hours of the final NaTPB strike.

The analytical data used to predict the Cs+, K+ and TPB- equilibrium solubility product constant will be determined as a function of temperature. The impact of the ratio of potassium to cesium, as well as the presence of organics and other ions on the equilibrium solubility constant will be determined.

Equations 1 and 2 then provide the ability to predict soluble Cs+, K+ and TPB- concentrations. Accurate process material balances can then be produced which reflect the minimum amount of NaTPB required to achieve the soluble Cs concentration desired. When combined with an understanding of soluble NaTPB decomposition (see 7.2.3.2) an additional amount of NaTPB can be included to maintain this decontamination level for the period required for processing.

7.2.3.2 Soluble NaTPB Decomposition Pathways

Following the unexpected benzene release during initial radioactive operations, a systematic program of tank sampling and laboratory testing was begun to understand the chemistry. A detailed report of these studies was issued on May 10, 1996 (reference 9). Key conclusions from this report are as follows:

- The major reaction which decomposed the excess NaTPB in Tank 48 occurred in November and December 1995. After consuming all of the excess NaTPB, the reaction subsided.
- The reaction consumed all of the available solid NaTPB in the tank, but no significant amount of insoluble potassium and cesium tetraphenylborate reacted.
- Benzene was the major product of the decomposition. Phenol and biphenyl were minor products, and phenylboronic acid was a semi-stable intermediate.
- The average rate of benzene generation in Tank 48 during the rapid decomposition reaction was at least 1,000 times faster than the current generation rate based on radioactive decay and the reaction of residual TPB decomposition products and may have been much greater at peak rates (reference 9).
- Laboratory tests with simulated waste have produced rapid decomposition of NaTPB similar to Tank 48 in stoichiometry, rate, and extent of reaction. These tests demonstrated that copper ion and sludge solids increase the rate of decomposition of tetraphenylborate slurries (reference 9).

Based on this work (and the understanding of TPB slurry hydrolysis from DWPF), the primary soluble TPB- decomposition reaction path is thought to be tetraphenylborate (TPB or 4PB) to triphenylboron (3PB) to diphenylboronic acid (2PB) to phenylboric acid (PBA or 1PB) to boric acid ($H_3 BO_3$) releasing a phenyl ring at each step producing primarily benzene but also producing phenol and biphenyl. The reactions are catalyzed by copper and other species.

Work to date has indicated that soluble copper may be the primary catalyst for the last two reactions in the decomposition chain (2PB to 1PB to $H_3 BO_3$), but does not fully explain the high generation experienced in Tank 48. Additional catalysts are being identified for the first part of the reaction chain. The reaction mechanisms described above will be confirmed or other mechanisms elucidated.

Based on the above reactions, solubility and kinetic expressions have been developed which match Tank 48 benzene generation. These expressions have been applied in material balances for ITP and the interface points with Late Wash and Saltstone. Parametric calculations determining the impact of tank temperature and amount of excess NaTPB have been conducted. These preliminary material balances are being used for Authorization Basis and design basis work which is proceeding in parallel with the chemistry program. Determination of an adequate safety basis will be an iterative process using the results of facility testing, analyses, and chemistry test results. The impact of this information on each safety strategy alternative will be used to choose a defensible safety basis which is robust and cost effective.

7.2.3.3 Catalyst Identification

These tests seek to identify and rank NaTPB decomposition catalysts or groups of catalysts. Potential catalysts which will be included in the test matrix are discussed in the test plan, Appendix A. Rates of NaTPB decomposition will be measured to assess the relative influence of specific catalysts.

Testing will be conducted in two phases. In the preliminary test phase, the influence of experimental test conditions (e.g., reaction vessel, agitation, salt solution composition) will be examined to define the best conditions for subsequent tests. The second experimental phase consists of statistically designed tests that focus on identifying key NaTPB decomposition catalysts.

A first step in this testing develops and verifies an essentially complete simulant which produces decomposition rates and temperature dependence similar to that observed in Tank 48H and provides the basis for further testing with simulants. Three groups of potential catalysts will be examined: organics, soluble metals and insoluble solids. Tests involving each group will introduce a number of similar species into the simulant at concentrations representative of those in ITP. Details of the species present and their concentrations may be found in the test plan for catalytic decomposition of soluble TPB, Appendix A. The exclusion of all three groups from the simulant renders an initial salt solution used to establish a baseline for the uncatalyzed NaTPB reaction rate. The inclusion of all of these groups in a test should provide a "fully-loaded" simulant of the ITP waste, and thus, should mimic the ITP NaTPB reactions. If a group is shown to include active catalysts, additional testing will be defined to identify the specific catalyst within the group.

As a matrix for the catalyst addition, the tests will use standard simulant solutions based upon data obtained in the preliminary phase of testing. The standard solutions are described in the applicable test plan. The preferred reaction temperature, vessel, ventilation, agitation, and sample frequency information will be determined from the preliminary tests and held constant for during the statistically designed tests.

Catalyst identification is essential to ensure that future production planning or flowsheet development minimizes catalyst concentration or provides for possible catalyst removal.

7.2.3.4 NaTPB Decomposition Kinetics

Testing with solutions which contain only Cu++, NaTPB, and caustic produced TPB decomposition rates much lower than observed in Tank 48. Testing is therefore required employing slurries which contain potential additional catalysts or which otherwise alter the physical configuration of Cu++ to increase catalytic activity.

The rate of NaTPB decomposition will be compared between the catalyst-containing simulant and the sum of the individual component testing. If these rates are similar to each other and Tank 48 then kinetic expressions will be developed for the reaction mechanism described.

If the catalyst identification studies suggest significant catalysts (in addition to copper) then additional kinetic testing for the individual components may be required, to develop appropriate kinetic expressions.

These kinetic expressions will be used to predict the benzene generation from soluble TPB decomposition using bounding conditions such as temperature and excess NaTPB as described above. This benzene generation rate will be added to the other known generation sources (i.e. radiolysis) for an "overall" generation rate. This predicted overall rate will then be compared to the preliminary rate and if necessary adjustments to the Safety Analysis Report and design basis documents will follow. The predicted overall rate will also be used as a comparitor for the actual waste confirming studies.

7.2.4 Solid TPB Decomposition

Milestone 5.2.2-2 requires the completion of tests to determine if insoluble TPB compounds contained in the ITP slurry can decompose at a significant rate under expected process conditions. The preponderance of data indicates that solid KTPB and CsTPB do not rapidly decompose under process conditions in ITP. However, concern over direct chemical degradation of solid KTPB was raised when higher than anticipated degradation was observed in early laboratory tests (references 9, 10). Further work is required under closely controlled conditions to determine if direct decomposition of solid phase KTPB and CsTPB is a significant mechanism for generating benzene under the conditions expected in the ITP and Late Wash processes. The test plan for stability of solid cesium and potassium tetraphenylborate is found in appendix B.

7.2.4.1 Solubility Studies

Tests (described in 7.2.3.2) will be conducted to determine solubility and equilibrium data for KTPB and CsTPB. KTPB and CsTPB solubilities will be determined as a function of ionic strength, temperature and ratio of potassium to cesium. The effect of salt solution composition (ionic strength) on CsTPB and KTPB solubilities will be determined. This work will allow the development of solubility correlations for use in modeling.

7.2.4.2 Solid Phase Reaction Modeling

A theoretical evaluation of potential solid phase and solution phase reactions will be performed to determine if direct decomposition of solid TPB compounds is significant compared to solution phase decomposition. This evaluation will consider the thermodynamic properties of the reactants and products of the reactions related to TPB decomposition.

Currently available solubility data, kinetic data on chemical degradation of soluble TPB, and kinetic data on radiolytic degradation of TPB will be used to model TPB degradation. The results of this modeling will be compared to observed data on the rate of increase of soluble Cs-137 during previous tests.

7.2.4.3 Solid TPB Decomposition Testing

Radioactive waste from Tank 48 will be used to develop improved baseline chemical kinetic data for solid phase KTPB decomposition. The effects of KTPB solids concentration, sodium molarity, excess soluble TPB, and temperature will be tested directly. Concentrations of intermediate decomposition products will be monitored to determine if they affect the observed results.

The goal of the radioactive waste testing is to determine under controlled conditions if decomposition of the solid KTPB can be achieved, and to identify the controlling parameters. The tests have been designed to provide an improved data baseline using real waste to provide the basis for designing the simulant studies.

After a baseline for solid KTPB decomposition has been obtained using Tank 48 waste, additional tests using non-radioactive simulant will be done to obtain kinetic data to refine the TPB decomposition model. The specific set of variables to be varied in the simulant tests will be determined as a result of the radioactive waste testing.

7.3 BENZENE RETENTION AND RELEASE

7.3.1 Issue Statement

The current scientific understanding of the mechanisms involved with the retention and release of benzene in the ITP System must be improved to ensure that measures to prevent benzene deflagration are adequate.

7.3.2 Resolution Approach

Measurements made during ITP Batch 1 indicate that significant quantities of benzene were retained within the liquid slurry (reference 9). The extent of this retention was significantly greater than solubility (reference 11). During pump operation, significant concentrations of benzene were released into the tank vapor space, but the benzene concentration rapidly decreased when pumps were turned off.

Continued benzene generation without periodic removal (e.g., pump operation) can potentially lead to a benzene layer near the liquid surface. Disturbance of the liquid surface would lead to benzene release by immediate evaporation. Such a phenomenon was likely observed in early March, 1996. The high release rate can lead to concentration gradients above the CLFL due to the evaporation rate exceeding the tank vapor space mixing. Understanding the retention and release mechanism provides information necessary to develop administrative controls and/or engineered features.

The physical and chemical basis for benzene retention and release will be characterized in a series of tests with simulant slurries. The postulated retention mechanisms include: solubility effects, formation of emulsions and rag layers, formation of free layers within the liquid phase, and benzene retention by the TPB solids. The primary factors that could lead to benzene release are diffusion, decrease in benzene solubility, changes in solution specific gravity, liquid additions, surfactants, and mechanical agitation (created by pumping or addition of liquids).

The studies of benzene retention and release are necessarily linked, and the work described in sections 7.3.5 and 7.3.6 will shed light on both retention and release. Current understanding suggests that more than one benzene retention mechanism is involved, depending to a large extent on benzene concentration in the slurry. The ease with which benzene is released, and hence the release rates attainable are related to the retention mechanisms.

The definition of the "apparent solubility limit" is key to understanding the retention and release tests. In a liquid-liquid solution with limited solubilities (such as water and benzene), the equilibrium vapor pressure of the benzene above the solution is less than the pure benzene vapor pressure at the same temperature as long as the solution is not saturated with benzene. When the solution reaches the saturation point (incipient two-phase liquid), the benzene vapor pressure over the solution is equal to the vapor pressure of a pure benzene phase. It has been observed that benzene can be retained in KTPB slurries at much higher concentration than in salt solutions. As benzene is added to a slurry, the equilibrium vapor pressure over the slurry increases until it reaches the vapor pressure of pure benzene (consistent with Henry's law). This is the point defined as the apparent solubility limit for benzene in the slurry.

At a concentration of benzene below the apparent solubility limit, there is defined relationship between the vapor and liquid concentrations of benzene. Better understanding of this domain requires determination of the vapor/liquid equilibrium constants. Other primary factors that need to be understood are the capacity of the slurry to retain benzene up to the apparent solubility limit, the effect of variable parameters on the retention capacity, and the concentration of benzene in the slurry when the apparent solubility limit is reached. Work on understanding the capacity for benzene retention and release in this domain is discussed in section 7.3.6, Benzene Retention and Release up to the Apparent Solubility Limit.

When benzene in the slurry exceeds the apparent solubility limit, it is postulated that the dominant retention mechanism may change. In order to control the process, it is necessary to understand the retention mechanism of benzene above the apparent solubility limit, and whether changes in the retention mechanism affect the ease of benzene release from the slurry.

Previous observations have led to the postulation of a "readily releasable" stage that is reached at very high slurry concentrations of benzene. At the readily releasable stage, the slurry may behave as if a pool of pure liquid benzene is present. Key questions that need to be answered regarding this domain are the dominant retention mechanism and the release rate that may be achieved.

The studies described in section 7.3.5 focus on determining the dominant retention mechanisms above the apparent solubility limit and determining the capacity of the slurry to retain benzene above the apparent solubility limit. Studies will attempt to identify characteristics associated with the readily releasable stage of benzene retention.

The effects of temperature, solids concentrations and surfactants on retention mechanism and capacity will be considered.

7.3.3 Postulated Retention Mechanisms

Liquid Solubility
Measurements of benzene solubility in simulated waste solutions, including NaTPB, have been made (reference 12). The dominant factor affecting solubility in these measurements has been the Na ion concentration and to a lesser extent, temperature. Surfactants are known to have an effect on solubility of immiscible systems. Low concentrations of surfactants, like tributyl phosphate, are used in ITP and related processes. Some NaTPB decomposition products may also behave as surfactants. Therefore, more tests of benzene solubility in slurry containing surfactants will be conducted. The additional tests will consider examining benzene solubility over the range of Na ion concentration, temperature, surfactant concentration, and decomposition product concentrations that are expected in the ITP process.

Emulsions and Rag Layers
Systems involving two liquid phases can form dispersions or emulsions which could increase benzene retention. With sufficient time, emulsions may coalesce into separate phases. However, systems containing particulates and other organic films typically inhibit coalescence and form "rag" layers. Formation of dispersions and emulsions has not been studied in previous testing with waste slurries at SRS. Tests will be conducted to determine whether benzene dispersions and emulsions form within simulated ITP waste slurry and filtrate. Surfactants and solids distribution may have a significant role in emulsion and rag layer formation and will be considered in the development of these tests.

Free Layers
Immiscible systems can form free layers either by coalescence of previously formed emulsions or by entrapment under a layer of material that forms a retentive barrier (reference 13). Such layers (rag layers and free layers) have been postulated as the explanation for the rapid release of benzene with an apparently non-uniform distribution that occurred in early March, 1996. Free layer formation has not been studied in previous testing with waste slurries at SRS. Surfactants and solids distribution may have a significant role in formation of these layers and will be included in the scope of these tests. Tests will be conducted to determine if formation of free layers is feasible with simulated ITP waste slurry and filtrate; and, if feasible, the conditions required to establish a free layer will be determined. Test development will consider salt concentration, surfactant concentrations, solids concentration, and benzene concentration. Once the conditions are defined, evaluations will be conducted to determine controls necessary to avoid those conditions that lead to rag layers and free layers as necessary to support development and implementation of the revised safety strategy.

Solids Retention
The TPB solids are expected to have an affinity to adsorb benzene and other organics within the waste slurry. Sludge solids may also have some potential for adsorption of organics. The benzene may have an affinity to form adherent coatings or droplets on the surface of the solids. Such coatings or droplets may result from macroscopic contact with benzene in the slurry or may result from growth or nucleation of adsorbed benzene. Molecules of benzene can form adsorbed layers on the solids or form molecular clusters or micelles. Preliminary testing indicates that TPB solids have some degree of involvement in benzene retention as evidenced by observed progressive decreases in benzene vapor pressure over solutions with increasing solids content (reference 11). Benzene retention by TPB solids will

be measured at Na ion concentrations and weight percent solids that cover the anticipated range of ITP operations. Surfactants may have a role in the formation of droplets and coatings and will be included in the development of these tests. Key solids retention mechanisms (adsorption, micelles, etc.) will be identified.

7.3.4 Postulated Release Mechanisms

The primary factors that could lead to benzene release are diffusion, decrease in benzene solubility, changes in solution specific gravity, liquid additions, surfactants, and mechanical agitation (created by pumping or addition of liquids). As the benzene retention studies proceed, other factors may be identified for evaluation. Each factor is briefly described below:

Diffusion
After the addition of salt solution and NaTPB for ITP Batch 1, benzene concentrations in the vapor space were less than 10-20 ppm in the Tank 48 vapor space when mixing pumps were not in operation. This was observed even when several thousand kilograms of benzene were present (reference 9). Thus, diffusion from the slurry is a minor factor in benzene release. Sufficient information is available from 1995-96 ITP plant operations to determine mass transfer coefficients for Tanks 48 and 50 in the unagitated state. This information will be evaluated and documented.

Decrease in Solubility
Benzene solubility decreases with lower temperatures and increased salt concentrations. Presence or absence of surfactants can change the solubility. Studies will be conducted to better quantify the effects of temperature, salt concentration, and surfactant additions on benzene solubility (see Sec. 7.3.5) and those results will be equally applicable to releases due to solubility changes.

Decreases in Solution Specific Gravity
At the start of the ITP precipitation cycle, TPB solids are suspended at or near the surface of the approximately 5 molar sodium salt solution (reference 14). This layer of solids is believed to impede benzene release by adsorption on solids, trapping of benzene bubbles or droplets, etc. At later stages in the process, the specific gravity of the precipitate slurry is reduced via washing and the solids will tend to settle. Tests will be conducted to determine the effect of solution specific gravity and frequency of mixing on benzene release rates (see section 7.3.5).

Liquid /Chemical Additions
Benzene releases that occurred during water additions in the 1983 ITP plant test were originally thought to be due to the release of trapped benzene that had been produced by radiation damage to excess NaTPB in the tank. The excess present as solid NaTPB receives a large radiation dose during the precipitation and filtration steps in the ITP process. Benzene produced during this time is locked into the TPB crystal lattice. During the washing step, water is added which dissolves the TPB crystal and thus releases the trapped benzene.

Recent work (reference 15) has shown that the expected radiolytic production of trapped benzene under conditions of ITP operation is 100 times slower than previously thought. Thus, the impact of liquid additions on benzene release will be due primarily to localized agitation from the stream of liquid disturbing the waste surface. Benzene releases that have occurred during previous liquid additions (e.g., flushes during maintenance activities) will be evaluated and documented. Liquid additions in ITP will be conducted under test controls to validate the expected impact of liquid addition. Details of this testing will be developed separately in preparation for milestone 5.2.4-3.

Mechanical Agitation
The fact that mechanical agitation will lead to significant increases in benzene release rates is well established (reference 9). Mechanical agitation by mixing pumps was very effective in the removal of benzene retained in the Tank 48 slurry. All of the benzene attributed to excess NaTPB decomposition was accounted for by vapor release sampling. Conservative computational fluid dynamics modeling shows that the ITP tanks will be well mixed at volumes up to 600,000 gallons which corresponds well with data obtained during the processing of batch #1. The volume of future batches will be limited to 600,000 gallons to ensure that retained benzene can be released via operation of mixing pumps. Future testing in Tank 48 is being considered to determine if adequate mixing can be demonstrated at higher tank volumes.

Mass transfer coefficients were developed from benzene vapor-liquid equilibrium data from Tank 48 (reference 16). Also, mass transfer coefficients were calculated for Tank 50, but limited data for Tank 50 prevented determination of accurate values (reference 16). Tank 48 and Tank 50 mass transfer coefficients will be revised as more plant data become available. The effect of tank volume, solids concentration, and energy input will be considered in the determination of mass transfer coefficients. Laboratory tests will be conducted to evaluate the effects of temperature, salt concentration (specific gravity), surfactant concentration, and solids concentration on vapor-liquid distribution and benzene release rates. Mass transfer coefficients will also be developed for Tank 49, or Tank 48 data will be used to provide bounding values for Tank 49.

The effect of seismic agitation will be evaluated to ensure benzene release by this mechanism is bounded by other mechanisms. The seismic evaluation does not involve laboratory testing.

7.3.5 Retention and Release Above the Apparent Solubility Limit

As mentioned above, the tests required to understand benzene release mechanisms are interdependent with those required to define retention mechanisms and capacity. Testing of benzene retention and release above the apparent solubility limit will address two goals. The predominant mechanisms for retention of benzene in ITP filtrate will be defined. The capacity and distribution of benzene anticipated to be retained in Tank 48 slurry will be determined as a function of controlling parameters (temperature, TPB concentration, frequency of agitation, presence of insoluble solids). As the retention mechanism is better understood, the related release mechanisms may be determined.

Three areas of testing will be pursued. The first will concentrate on the development and application of direct methods for observing benzene retention in slurries. The second will provide a series of "bottle tests", bench scale tests which vary key parameters and measure the effect on benzene retention. The third will provide a large scale demonstration to measure retention capacity and identify any effects of scaling on retention.

Direct Observation of Retained Benzene
Potential observational methods include (but are not limited to) optical microscopy, ultraviolet microscopy, and magnetic resonance imaging, utilizing benzene specific dyes as appropriate. These methods will be pursued to provide direct observation of benzene in liquids and slurries. The methods will also provide support to the following tasks.

Bench Scale Tests for Benzene Retention
A series of tests will determine benzene retention capacity and releasability as benzene is accumulated beyond the apparent solubility limit. Tests will be performed without agitation of the slurries. The effect of time, temperature, and KTPB concentration will be determined. Testing will be performed at increasing benzene accumulation levels in an attempt to achieve benzene release rates consistent with those observed in Tank 48 in March, 1996. During these tests, the direct observation methods described above (and other appropriate measurements) may be applied to define retention mechanisms and capacities under the various conditions. At the end of quiescent periods in these tests, release testing will be performed to characterize relative release rates as a function of conditions.

Benzene Retention Demonstration
A limited set of pilot scale tests will be performed to determine the effect of scaling on benzene retention mechanisms and capacity. These tests will focus on the retention behavior over a period of one to two months (bounding the operational time period that a tank might go without agitation). At least one test series will be continued over a longer period to determine if there is a qualitative change in retention behavior over time. During these tests, the direct observation methods described above (and other appropriate measurements) will be applied to define retention mechanisms under the various conditions.

The results of the above tests will be used to define bounding benzene retention capacities for ITP tanks under various conditions, and to define the acceptable range of operating conditions. The details of the test plan to define the important benzene retention mechanisms (Milestone 5.2.3-1) and to determine the capacity and distribution of benzene retention in Tank 48 slurry as a function of controlling parameters (Milestone 5.2.3-2) may be found in Appendix C.

7.3.6 Retention and Release up to the Apparent Solubility Limit

Tests addressing benzene retention and release up to the apparent solubility limit will determine the apparent solubility and slurry/vapor equilibrium ratios for KTPB slurries as a function of temperature, salt solution composition and concentration. Tests will also determine if insoluble solids, absorbed radiation dose, decomposition intermediates, surfactant concentrations or aqueous specific gravity have significant effects.

Details of the tests involving benzene retention and release up to the apparent solubility limit will be provided as the test plan for benzene release studies (Milestone 5.2.4-1), and may be found in Appendix D. Completion of the work to define benzene release mechanisms will include calculation of bounding mass transfer coefficients for ITP tanks (Milestone. 5.2.4-2).

The effect of water addition and tank dilution on slurry benzene retention will be tested. This retention information is needed to understand mechanisms that can lead to immediate benzene release or release during pump operation. The experimental details for this test series have not yet been defined. The benzene release rates due specifically to localized agitation from water or chemical additions will be reported in Milestone 5.2.4-3. The results of these studies will be combined with the results of the retention test to determine the bounding quantities of benzene that could be retained in and released from waste slurries under various conditions (Milestone 5.2.4-4).

The combined results of all testing for benzene generation, retention and release, as well as the confirmatory studies performed on real waste material, will be used to complete calculations documenting the bounding benzene generation, retention and release rates (Milestone 5.2.1-1). These rates will be compared to the bounding values used to initiate development of the Safety Analysis Report to confirm the validity of the Authorization Basis before initiating facility operations.

7.4 REAL WASTE TESTING

Key elements of the testing described above will be confirmed with appropriate testing using real waste. The first set of real waste studies will simulate, to the maximum extent reasonable, the actual conditions that will be encountered in the next phase of real waste processing. Waste samples will be obtained from the tanks to be processed during cycle 1, batches 2, 3, and 4 of ITP processing. Parameters such as temperature and TPB concentrations will be selected to provide conditions similar to, or credibly bounding those to be encountered in the processing steps. Since the real processing will occur in three batches, the tests will be performed sequentially for the three waste samples to be tested. The behavior of benzene, Cs, and appropriate intermediates will be monitored.

Two more sets of real wastes tests are planned to observe behavior under more bounding conditions. Other changes, such as the use of additional waste types or additional sludge solids, are still being defined. The expectation is that the behavior observed during simulant testing will be confirmed with real waste. Detailed requirements for the second and third set of real waste tests will be developed based on the results of simulant testing. The details of the real waste test plan will be provided in Appendix E.

The combined results of all testing for benzene generation, retention and release, as well as the confirmatory studies performed on real waste material, will be used to complete calculations documenting the bounding benzene generation, retention and release rates (Milestone 5.2.1-1). These rates will be compared to the bounding values used to initiate development of the Safety Analysis Report to confirm the validity of the Authorization Basis before initiating facility operations.

8.0 WORK CONTROL AND RESPONSIBILITIES

8.1 APPLICABLE PROCEDURES

Site-wide and lower level procedures have been established at WSRC to assure the quality of completed tasks that provide information related to the validity of, or changes to, a technical baseline for equipment and processes at the Savannah River Site. For the research and development work to be done as a part of this test program, and in the discussion below for specific procedures, ITP Engineering functions as the Design Authority, while the Savannah River Technology Center (SRTC) functions as the Technical Agency. Key applicable Quality Assurance Procedures (QAPs) and the lower tier implementing procedures controlling the research and development tasks performed by a Technical Agency at the request of a Design Authority are grouped by the manual containing them and are summarized below.

8.1.1 WSRC 1Q - Quality Assurance Manual (reference 17)

- QAP 2-3 (Rev. 1), "Control of Research and Development Activities"

  In QAP 2-3, R&D is designated a task if it produces information that will become part of a Technical Baseline as defined in the E7 Manual, "Conduct of Engineering and Technical Support", or if it is designated as a task by a requester or a research and development Level 3 manager. A Task Technical Plan and a QA Task Plan to cover designated tasks are required for information that will be developed as part of the Technical Baseline. Section 8.0 of this QAP describes requirements for writing a Task Technical Plan (TTP) and the requirements for a QA Task Plan.

- QAP 2-7 (Rev. 1), "Program Requirements for Analytical Measurement Systems"

  This procedure applies to WSRC analytical measurement organizations which control their measurement systems and equipment with a documented Measurement Control Program. Other measurement and test equipment is calibrated against traceable standards, and periodically checked to establish if recalibration is needed.

- QAP 12-1 (Rev. 5), "Control of Measuring and Test Equipment"

  This procedure defines the requirements and responsibilities for the control of Standards and Measuring and Test Equipment (M&TE) used to support WSRC activities.

8.1.2 WSRC E7 - Conduct of Engineering and Technical Support Manual (reference 18)

- Procedure 2.02 (Rev. 0), "Baseline Technical Task Request (U)"

  This procedure describes the preparation of a TTR by a Design Authority that requests technical services or information from a Technical Agency related to the validity of, or changes to, a technical baseline.

- Procedure 2.40 (Rev. 0), "Design Verification and Checking (U)" and Procedure 3.60 (Rev. 1), "Technical Reports (U)"

Procedure 2.40 describes a procedure for independently verifying and checking an engineering document for accuracy against specified requirements by a Technical Agency that develops the document. Together with Procedure 3.60, it provides the requirements for document results in a technical report.

8.1.3 WSRC L1 - Savannah River Technology Center Procedures Manual (reference 19)

- Procedure 4.19 (Rev. 3), "Technical Notebook Use (U)"

  This procedure describes controls and guidance for using technical notebooks to record technical work activities.

- Procedure 7.10 (Rev. 0), "Control of Technical Work (U)"

  This procedure provides guidance in the use of procedures contained in the E7 manual at SRTC.

- Procedure 8.01 (Rev. 1), "SRTC QA Program Implementation (U)" and Procedure 8.02 (Rev. 3), "SRTC QA Program Clarifications (U)"

  These two procedures establish the system used to implement the WSRC Manual 1Q within the SRTC, including clarifications, expansions or definitions needed to fully implement the 1Q requirements.

- Procedure 8.17 (Rev. 0), "QA Records Management (U)"

  This procedure establishes the requirements to identify, authenticate, receive, index, store, preserve, retrieve, correct, and dispose of documents designated as QA records.

8.1.4 Supporting Analytical Procedures

The Analytical Development Section (ADS) of SRTC provides direct analytical support (i. e., chemical analyses) for routine plant sample analysis, non-routine plant sample analysis, and samples supporting research and development tasks performed at SRTC.

- WSRC Manual L16.1 - Analytical Development Section Analytical Operating Procedures (reference 20)

  Analytical operating procedures used by the ADS for routine analytical methods are contained in this manual. Procedural controls, instrument calibrations, quality checks, and standards used for these routine methods are controlled by ADS. Quality assurance of these routine methods are implemented in accordance with QAP 2-7.

- Exploratory and Customer-Assisted Analytical Procedures

  Exploratory and customer-assisted analytical procedures are used by ADS when an analytical method is not sufficiently mature to be adopted as a routine procedure for inclusion in Manual L16.1. For exploratory and customer-assisted procedures, ADS has developed analytical procedure sufficiently to offer the analysis on a non-routine basis only. Blind standards and calibration standards are used in conjunction with these non-routine analyses to assure the quality of the results. The processes that ensure the quality of non-routine analyses are described in the specific Task QA plans. ADS personnel normally prepare standards for exploratory procedures as part of the procedure development. Customers submitting samples for analysis also prepare and submit standards to ADS for customer-assisted procedures.

8.2 CONTROLS AND RESPONSIBILITIES

8.2.1 Work Controls

- Preparation of TTRs

  In accord with WSRC procedures, a series of Technical Task Requests (TTRs) will be prepared that formally request technical assistance for services or information related to the validity of, or changes to, the technical baseline for the ITP process. After a completed TTR is approved, it will be forwarded to SRTC for their review and acceptance of the task(s) specified in the TTR. Key tasks and key parameters will be specified in the TTRs.

- Preparation of TTPs and Task QA Plans

  After a TTR is accepted by SRTC, a Task Technical Plan (TTP) and a Task Quality Assurance (QA) Plan will be prepared, reviewed and approved by SRTC. The TTP formally describes the plan to be followed in the performance of a task to obtain data and information that will be delivered to ITP Engineering in response to the TTR. The Task QA plan defines and documents the QA controls to be implemented to assure both the validity of data and the satisfaction of the requester's requirements. As information is developed, revision of a TTP may be necessary. Concurrence with a proposed change is required and the revised TTP must be prepared by SRTC and approved by SRTC and ITP Engineering.

  A TTP shall contain sufficient experimental detail (e.g., ranges of experimental conditions to be tested, description of controls, analytical procedures, equipment) to assure that results obtained will provide the technical information needed for the necessary control and understanding of the ITP process.

- Documentation of Experimental Results

  Instructions, supporting information, experimental conditions and experimental data generated to complete the described tasks will be recorded in bound, numbered technical notebooks. All work shall be done in accord with the approved TTP. Upon completion of the required experimentation, results will be documented in a separate technical report. The report becomes part of the technical baseline upon formal approval by ITP Engineering.

8.2.2 Responsibilities

TTRs will be prepared by cognizant personnel representing ITP Engineering. The responsible manager in the ITP Engineering organization must approve a TTR before it will be transmitted to SRTC.

For the tasks supporting this plan, a TTP prepared in response to a TTR will be prepared by a lead scientist or engineer assigned to perform the tasks. The TTP is peer-reviewed at SRTC for technical adequacy, approved by the SRTC Level 3 Manager (or his designee) and submitted to the ITP Engineering manager (or his designee) for review and approval. After review and concurrence by cognizant personnel within the ITP Engineering organization, the ITP Engineering manager approves the TTP for the tasks supporting the original TTR.

In conjunction with a TTP, a Task QA Plan is separately documented by the lead scientist that prepared the TTP. Approval of the Task QA Plan prepared in support of a TTP must be approved by the SRTC Level 3 Manager (or his designee) and the SRTC Cognizant Quality Function (CQF). Review and concurrence by ITP Engineering with the Task QA Plan shall also be documented.

SRTC will perform the tasks described in the TTRs in accordance with the approved TTP. The lead scientist or engineer assigned to a task is responsible for maintaining technical notebooks and preparing any Technical Reports based on the experimental work.

Draft Technical Reports that provide the information requested by a TTR will be prepared, peer-reviewed by SRTC, and approved for formal review by ITP Engineering. After all comments on the draft report have been satisfactorily resolved, Technical Report(s) will be formally approved by SRTC for issue.

9.0 References

1. Department of Energy Implementation Plan for DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 96-1 TO THE SECRETARY OF ENERGY, Revision 0, October 1996.

2. Radioactive Operations Commissioning Test Program, HLW-ITP-95-0240.

3. Tank 48 and Tank 50 Liquid Phase Thermal Analysis for Cycle 1 (U), WSRC-TR-95-0220, K. C. Kwon, September 14, 1995.

4. Analysis of Benzene Formation During PVT-1 Oxalic Acid Filter Cleaning, HLW-ENG-960021, Rev. 1, G. Morin to T. Lex, September 9, 1996.

5. Benzene Release Rates During ITP Accidents, WSRC-RP-93-944, D. Walker to S. Fink, July 6, 1993.

6. L. Lee and L. Kilpatrick, DP-1636, A Precipitation Process for Supernate Decontamination, November 1982.

7. E. Siska, *Magyar Kemiai Folyoirat*, 82, 275 (1976).

8. P. Debye and E. Huckel, *Physik.* Z., 24, 185 (1923).

9. D.D. Walker, M.J. Barnes, C. L. Crawford, R.F. Swingle, R.A. Peterson, M.S. Hay and S.D. Fink, *Decomposition of Tetraphenylborate in Tank 48H* (U), WSRC-TR-96-0113, Rev. 0, May 10, 1996.

10. D.D. Walker and C.A. Nash, *Results from Tank 48H Slurry Decontamination and Decomposition Experiments in Support of ITP Process Verification Testing* (U), WSCR-TR-96-0190, September, 1996.

11. Vapor Pressure of Benzene, Methanol and Isopropynol Over Salt Solutions, DPSE-88-661, D. D. Walker to G. T. Wright, March 28, 1989.

12. Sodium Tetraphenylborate Solubility and Dissolution Rates, WSRC-TR-95-0092, M. J. Barnes et al., to S. D. Fink, March 7, 1995.

13. Composition of Washed and Unwashed In-Tank Precipitation (ITP) Solids, WSRC-RP-96-7, L L. Kilpatrick to S. D. Fink, July 16, 1996.

14. Parameters of Tetraphenylborate Slurry Phase Separation, WSRC-RP-94-1333, R. A. Peterson to S. D. Fink, December 27, 1994.

15. Radiolytic Production of Trapped Benzene, WSRC-TR-96-0141, D. D. Walker to S. D. Fink, June 5, 1996.

16. Initial Estimates of Mass Transfer Coeffcicients in Tank 48H and Tank 50H, WSRC-TR-96-256, R. A. Peterson et al., to S. D. Fink, August 16, 1996.

17. Quality Assurance Manual (U), Westinghouse Savannah River Company Procedure Manual 1Q.

18. Conduct of Engineering and Technical Support (U), Westinghouse Savannah River Company Procedure Manual E7.

19. Savannah River Technology Center Procedures Manual (U), Westinghouse Savannah River Company Procedure Manual L1.

20. Analytical Development Section Analytical Operating Procedures (U), Westinghouse Savannah River Company Procedure Manual L16.1,Vol's I to IV.

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APPENDIX A:

TEST PLAN FOR CATALYTIC DECOMPOSITION OF SOLUBLE TETRAPHENYLBORATE

DNFSB 96-1 IMPLEMENTATION PLAN COMMITMENT #3, MILESTONE #5.2.2-1

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1.0 Introduction & Background

The In-Tank Precipitation (ITP) facility at the Savannah River Site initiated radioactive operation in Tank 48H in September 1995. During pump operation in December 1995, benzene evolved from Tank 48H at higher rates than expected, though the operational safety limit was never approached. Subsequent investigations revealed the source of benzene was catalytic decomposition of excess, soluble tetraphenylborate (TPB) present to assure adequate suppression of cesium solubility.[7.1]

In August, 1996 the Defense Nuclear Facilities Safety Board (DNFSB) issued Recommendation 96-1 in which the Board recommended operation and testing not proceed without an improved understanding of the mechanisms of benzene generation, retention, and release. In the 96-1 Implementation Plan,[7.2] the Department of Energy developed its approach to resolve the issues raised by the DNFSB. The plan is based on the development of a revised safety strategy and a combination of bench, pilot scale and plant tests aimed at understanding benzene generation, retention, and release. Further, the test program includes these elements:

- Benzene generation
  + determine catalyst(s), mechanisms, and rate constants for decomposition of soluble TPB
  + study stability of solid CsTPB and KTPB
  + confirm using actual wastes

- Benzene retention
  + determine capacity of slurries to retain benzene
  + endeavor to understand the physical forms in which benzene is retained

- Benzene release
  + develop an understanding of how benzene is released in lab scale tests and in pilot scale demonstration
  + determine plant equipment mass transfer coefficients in plant tests

Implementation Plan Commitment # 3 states that an overall bounding benzene generation rate will be determined and documented based on the understanding of all major generation mechanisms. Milestone #5.2.2-1 requires a test plan for catalytic decomposition of soluble TPB to be issued December 1996. This test plan describes the basis for determining the primary catalyst(s), the reaction mechanisms, and rate constants necessary to understand and describe the decomposition of soluble TPB.

2.0 Scope

The scope of this test plan covers the activities performed by the Savannah River Technology Center (SRTC). These activities will determine the primary catalyst(s) and reaction mechanisms for the catalytic decomposition of soluble TPB.

Significant tests have already been performed. In Reference 7.1, Walker *et al.* report the results from tests using radioactive Tank 48H materials and other radioactive wastes. Multiple sources of sodium TPB (NaTPB) and non-radioactive simulants of limited composition were also tested. Parameters tested included temperature, soluble copper (Cu), sludge solids, and NaTPB.

Testing reported by Barnes and Edwards[7.3] studied "clean" solutions which included only Cu, NaTPB, and caustic (NaOH) and which produced TPB decomposition rates approximately three orders of magnitude lower than observed in Tank 48H. To assure adequate understanding of soluble TPB decomposition, the scope of testing has been broadened to include these elements:

- develop and test an essentially complete simulant (also known as the "all-inclusive" simulant[1]) which produces decomposition rates similar to or greater than those observed in Tank 48H and provides the basis for further testing with simulants,

- perform tests to identify the primary catalyst or groups of catalysts, and

- perform tests to determine the primary reaction mechanisms and the rate constants for TPB decomposition including the intermediate reactions.[2]

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[1] The "all-inclusive" simulant is as complete as possible based on analyses of Tank 48H, Batch 1 as reported in Reference 8.1; particularly with respect to potential catalyst species. For the remainder of this document, this simulant will be referred to as Tk 48H, Batch 1 simulant. See Section 4.2.1 for a listing of potential catalyst species.

[2] The proposed primary reaction path is tetraphenylborate (TPB or 4PB) to triphenylboron (3PB) to diphenylborinic acid (2PB) to phenylboric acid (1PB) to boric acid (H_3BO_3) releasing a phenyl ring at each step producing primarily benzene but also producing phenol and biphenyl.

3.0 Objectives and Expectations

3.1 Objectives: The test objectives are designed to develop a more fundamental and quantitative understanding of the decomposition of soluble TPB and the consequent generation of benzene. A Technical Task Request (TTR)[7.4] has been issued by ITP Engineering (ITP-E) defining the specific tasks for this plan. Stated tasks are:

3.1.1 Perform tests to demonstrate a Tk 48H, Batch 1 simulant which produces rates similar to or greater than those observed in Tank 48H.

3.1.2 Determine significant reaction mechanisms and rate constants with soluble Cu catalyst as a function of temperature, hydroxide concentration, reactant and intermediates concentrations.

3.1.3 Perform preliminary testing to develop candidates for catalyst ID testing; include trace soluble species, sludge solids, sodium titanate, and organics.

3.1.4 Based on preliminary catalyst ID testing, perform statistically designed experiments to identify the primary catalyst(s).

3.1.5 Determine the effect of active catalysts on decomposition rates of TPB and the reaction intermediates.

3.1.6 Provide correlations and rate constants for use in modeling the decomposition reactions and the process flow sheet.

3.2 Expectations: At the conclusion of testing under this plan, it is expected that:

3.2.1 A Tk 48H, Batch 1 simulant will be developed to serve as the basis for further testing with simulants. Previous decomposition rates observed in Tank 48H will be used to confirm the simulant is satisfactory for further testing. If noble metals are key catalysts, the simulant decomposition rates might be higher because 1) noble metals were not detected in the Tank 48H sludge solids, and 2) the sludge simulant contains the maximum noble metals expected.

3.2.2 The active catalyst specie(s) will have been identified. The testing is initially intended to determine the catalyst(s) for TPB decomposition based on the fact that previous work indicates the 3PB, 2PB, and 1PB decomposition rates may be accounted for by soluble copper alone. If data indicates more rapid intermediates decomposition than is attributable to soluble copper, additional testing may be required to determine the active catalyst(s) for the intermediates reactions.

3.2.3 Important parameters such as temperature and composition (including catalyst(s), reactants, and intermediates) will be varied such that TPB decomposition, the reaction intermediates, and benzene generation can be adequately predicted. Use of the data includes evaluation of operating scenarios, benzene generation terms for safety analyses, retention/release calculations, and permits, and, along with new Cs solubility data, determination of the minimum NaTPB addition requirements.

3.2.4 Parameters such as sodium concentration and temperature will be varied such that results are applicable throughout the ITP and Late Wash processes, including Saltstone feed storage.

4.0 Test Methodology and Approach

4.1 Key parameters must be selected and/or controlled to produce the expected results. The key parameters are temperatures, compositions, and test conditions.

4.1.1 Temperature is an extremely important parameter since previous testing indicates that observed TPB decomposition is a stronger function of temperature than typical, uncatalyzed chemical reactions. Based on reported activation energies,[7.1,7.3] the TPB reaction rate doubles every 4 to 6°C as compared to the "typical" rate of doubling every 10°C. Selected test temperatures must: 1) be high enough to produce measurable decomposition in a reasonable period of time, 2) span or bound safety basis temperature limits, and 3) provide sufficient information on temperature dependence to evaluate operation at temperatures which produce very low decomposition rates.

Current plans for future ITP operation include safety basis temperature limits of 40 °C and operating limits of 35 °C for all operations except Late Wash. Startup testing indicates Late Wash may operate at temperatures as high as 65 °C unless additional process cooling is provided. Previous work shows tests performed at 50 °C or higher produce reasonably rapid and measurable decomposition. Temperature dependence of the rate constant is evaluated by obtaining the slope and intercept from a plot of reciprocal temperature (1/T(°K)) versus the natural log of the rate constant (ln k). The intercept is the pre-exponential factor (a) and the slope is the activation energy (E_a) in the Arrhenius equation

$$k = a\, e^{-(E_a/RT)}$$

Three points are sufficient to assure a good fit and to allow extrapolation with confidence, especially to lower temperatures where the rates are low enough to make experiments impractical.

Typically temperature dependence will be determined by testing at three temperatures in the range of 40 to 70 °C.

4.1.2 Compositions must be selected to assure relevance to the process and to maximize experimental productivity. Test compositions are selected based on documentation of previous process samples and test objectives. The experimenters define and document the compositions in the Task Technical Plans which are reviewed and approved by ITP Engineering and the ITP Flow Sheet Task Team. Test solutions and slurries are submitted for analyses prior to initiation of the experiments to assure the starting compositions are known and on target.

4.1.3 Test conditions such as agitation, vessel material, cover gas, *etc.*, may affect experimental results. Test conditions which may affect results will be explored as part of NaTPB Decomposition Catalyst Identification Studies (see 4.2.2) and will be appropriately specified in future studies. With the exception of cross check experiments (see 5.2.1), there are no plans to explore or quantify any effect due to cover gas composition; that is, N_2 versus air versus N_2 diluted air (~5% O_2). Walker and Nash reported air causes an induction period for NaTPB decomposition but no reported delay in the onset of reaction with a N_2 atmosphere. If the induction period is ignored, the decomposition rates are similar.[7.5]

4.2 Testing for this test plan will be performed under three Task Technical Plans (TTPs) prepared by the performing organization. The TTPs contain detailed information on methods, temperatures, compositions, test conditions, and analytical requirements. The TTPs are summarized below.

4.2.1 Decomposition Studies of Tetraphenylborate Slurries - C. L. Crawford[7.6]

Tests using the Tk 48H, Batch 1 simulant have the primary objective of demonstrating TPB decomposition rates similar to or exceeding rates observed in Tank 48H. The simulant composition is based on analyses of Tank 48H material reported in Reference 7.1. The Tk 48H, Batch 1 simulant will include soluble salt components, soluble and insoluble NaTPB and KTPB solids, soluble metal ions, trace organic species, simulated sludge solids, and monosodium titanate (MST). Table 1 shows the target concentrations of the potential catalysts which will be included in the initial testing of the Tk 48H, Batch 1 simulant. Individual candidates have been ordered within each group to reflect the initial estimate of relative catalyst activity.

Tests will be performed at three temperatures to determine the temperature dependence. The important parameters to control are the starting simulant compositions and the test temperatures.

Testing of a scoping nature will also be performed in parallel with the above tests to obtain an early indication of the effect of removing insoluble solids from the salt solution. Slurries without sludge and/or MST will be tested.

Table 1

Organic Compounds (target concentration)	**Soluble Metals (target concentration)**	**Insoluble Solids (target concentrations)**
2PB (125 mg/L)	copper (II) (1.7 mg/L)	copper (2 mg/L)[a]
benzene (720 mg/L) phenol (125 mg/L)	ruthenium (III) (0.8 mg/L) rhodium (III) (0.2 mg/L) palladium (II) (0.4 mg/L) silver (I) (0.6 mg/L)	ruthenium (4.6 mg/L)[a] rhodium (1.2 mg/L)[a] palladium (2.2 mg/L)[a] silver (6.2 mg/L)[b]
biphenyl (150 mg/L) PBA (125 mg/L) 3PB (125 mg/L) diphenylmercury (150 mg/L)	iron (III) (2.6 mg/L) chromium (VI) (60 mg/L)	mercury 80 (mg/L)[b]
isopropanol (50 mg/L) methanol (5 mg/L)	mercury (II) (2.2 mg/L) cadmium (II) (0.4 mg/L) zinc (II) (8.8 mg/L) molybdenum (VI) (12 mg/L) cerium (IV) (0.3 mg/L)	MST (2 g/L) manganese (118 mg/L) iron (576 mg/L)[a] chromium (4 mg/L)[a] uranium (172 mg/L)[a] nickel (50 mg/L)[a]
	silicon (IV) (16 mg/L) selenium (VI) (1 mg/L) arsenic (IV) (0.04 mg/L) lead (II) (1.2 mg/L) tin (II) (2.1 mg/L) cobalt (II) (0.04 mg/L) calcium (II) (12.2 mg/L) strontium (II) (0.1 mg/L) lanthanum (III) (0.05 mg/L)	aluminum (96 mg/L)[a] magnesium (2 mg/L)[a] zinc (4 mg/L)[a] zirconium (50 mg/L)[a] lead (6 mg/L)[a]

[a] Based on sludge concentration of 2 g/L.
[b] These components are included in testing described in Section 4.2.2.

4.2.2 Sodium Tetraphenylborate Decomposition Catalyst Identification Studies - M. J. Barnes[7.7]

Tests to identify catalysts are to be performed in phases. In phase one, tests will be performed to define the best conditions (*e.g.* glass vs. carbon steel vessel, sealed vs. purged, agitated vs. unagitated) for performing subsequent statistically designed experiments. Phase one tests will include 1) cross checks of two previous similar tests which produced different results, 2) tests using the Tk 48H, Batch 1 simulant at varying conditions to determine the best conditions for subsequent experiments, and 3) a screening test to determine if noble metals might be the principal catalysts.

For the second phase, the TTP will be revised to specify the conditions for statistically designed tests of the Tk 48H, Batch 1 simulant recipe. These tests will identify the catalytic significance of the major potential groups: organic additives, trace soluble metals, and insolubles (sludge and MST). Results of the initial statistically designed experiments will be evaluated and, if needed, the TTP will be revised to add statistically designed experiments to further identify the primary catalyst(s).

For the preliminary testing, the most important parameters requiring control are the starting simulant compositions and the test temperatures. Specification of additional parameters and conditions may result from the preliminary testing.

4.2.3 Decomposition Studies of 3PB, 2PB, and 1PB in Aqueous Alkaline Solutions Containing Copper - C. L. Crawford[7.8]

The first step toward describing the TPB decomposition mechanisms and rate constants is to follow the decomposition of the intermediates in a simplified, "clean" system. Tests will be performed in parallel with other tests in this plan and will start with each intermediate (3PB, 2PB, and 1PB) in a statistically designed matrix to study the effects of temperature, NaOH concentration, and Cu concentration. This study will be an extension of Barnes' studies documented in Reference 7.3. Once more, the key parameters to control are the starting simulant composition and the test temperatures.

4.3 Based on the rates measured in the 3PB/2PB/1PB testing (Section 4.2.3) as compared to rates observed in Tank 48H and other tests, additional 3PB/2PB/1PB testing with the Tk 48H, Batch 1 simulant catalysts (soluble metal species, trace organics, and insoluble solids) may be performed. If this testing is necessary, a separate TTP will be prepared.

5.0 Test Descriptions

5.1 Decomposition Studies of Tetraphenylborate Slurries[7.6]

5.1.1 Twelve test slurries will be prepared from a concentrated salt matrix containing potassium plus nine sodium salt components. Similar to the composition in Tank 48H during the rapid TPB decomposition, the Tk 48H, Batch 1 simulant contains sufficient NaTPB to produce a 4.5 wt.% slurry of KTPB, saturate the solution with NaTPB and have 1.5 wt.% insoluble NaTPB. The complete complement of potential catalysts will be added to six of these slurries: soluble organic additives, soluble metal species, and insoluble solids including simulated sludge with noble metals and MST (see Table 1). Six tests will be run with the Tk 48H, Batch 1 simulant, four with sludge and/or MST omitted, and two controls without the complement of potential catalysts (Table 2). Experiments will be performed at temperatures ranging from 40 to 70 °C. After preparation of the slurry, samples will be submitted to provide measurement of the starting composition.

Table 2

Temp	Complete	w/o Sludge and MST	w/o Sludge	Control
Low	X,X			
Mid	X,X	X	X	X
High	X,X	X	X	X

X indicates a test

5.1.2 The slurries will be placed in clean, sealed vessels and then maintained unstirred in a temperature controlled environment. The temperature will be maintained at setpoint ± 2 °C.

5.1.3 The vessels will be removed periodically to sample both the vapor and the slurry to follow the progression of the reaction. The frequency will initially be approximately 2 to 3 days but may be adjusted up or down based on how fast or slow the reactions are occurring. Upon removal, the vessel will be cooled in a water bath to room temperature. Prior to sampling, the vessel will be weighed and then shaken vigorously. Both the vapor and the slurry will be sampled, air injected to replace the volume withdrawn, and then the vessel weighed again prior to returning it to the controlled temperature environment.

5.1.4 Benzene will be measured in the vapor sample and in the slurry; a portion of the slurry sample is used for this purpose. The remaining portion of the slurry is filtered and the filtrate analyzed for soluble TPB, soluble organics, soluble boron, and possibly for soluble metals.

5.1.5 Testing will proceed until sufficient data is gathered to determine decomposition rates of TPB and the intermediates for each test slurry.

5.2 Sodium Tetraphenylborate Decomposition Catalyst Identification Studies[7.7]

The preliminary testing specified in the TTP includes cross checks of previous studies, determination of important test conditions, and screening of noble metal catalysts.

5.2.1 Two cross checks will be performed to provide insight into the effects of test conditions such as container material, agitation, etc.. The first cross check will use a slurry composition from previous testing.[7.7] The previous tests were performed in glass reaction vessels stirred and continuously purged with N_2 while being maintained at 50 and 70° C. The cross check will be performed using the same simulant and temperatures in sealed, unstirred carbon steel vessels. The second cross check will be of tests conducted in the Decomposition Studies of Tetraphenylborate Slurries (section 5.1). The cross check will use the Tk 48H, Batch 1 simulant at the mid and upper temperatures of the temperature range but in glass reaction vessels continuously stirred and purged with N_2.

5.2.2 Further evaluation of important test conditions will be performed using the Tk 48H, Batch 1 simulant. Tests will evaluate reaction vessel (carbon steel vs. glass serum bottles which are preferred for statistical testing), salt composition at Na concentrations which cover the range from ITP to Late Wash, and agitation (stirred vs. unstirred). All tests in this portion will be performed in the presence of air and at 55 °C.

5.2.3 Screening tests of potential noble metal catalysts will be performed in unstirred carbon steel vessels in the presence of air at 55 and 70°C. The trace organics, insoluble sludge and MST solids, and soluble metals will be omitted from the Tk 48H, Batch 1 simulant and only noble metals added to provide initial information on their catalytic activity.

5.2.4 The remainder of the experimental procedure essentially duplicates the steps detailed in sections 5.1.3 through 5.1.5.

5.2.5 Based on the information obtained in the previous test steps, the conditions (temperature, vessel, agitation, ventilation, sample frequency) for the statistically designed experiments will be selected. These conditions will be specified in a revision to the TTP. The initial statistically designed experiment has already been determined.[7.7] This experiment consists of twelve tests including a full replicate of six combinations of the Tk 48H, Batch 1 simulant and added organics, soluble metals, and/or insoluble sludge and MST solids. At the completion of the initial statistical tests, the data will be evaluated and, if needed, additional statistical tests designed and conducted to further isolate and identify key catalyst(s).

5.3 Decomposition Studies of 3PB, 2PB, and 1PB in Aqueous Alkaline Solutions Containing Copper[7.8]

5.3.1 Ten tests will be performed for each of the intermediates, a total of 30 tests, based on a statistically designed experiment which will study the main effects of four parameters with two center points to provide a replicate and an opportunity to check for non-linear response. In each set of ten, the four parameters to be studied are temperature, the intermediate, the hydroxide concentration and Cu concentration. Ranges to be tested are: temperature - 40 to 70°C, intermediates concentration - 100 to 2000 ppm, hydroxide - 0.5 to 2.5 M, and Cu^{+2} - 0.1 to 10 ppm.

In addition, two vessels containing various amounts of the intermediate will be prepared without Cu and stored at room temperature. These will provide controls to indicate the stability of the organic component in alkaline aqueous solution at room temperature. Initial samples of all test solutions will be submitted to provide starting measurements.

5.3.2 Same as 5.1.2

5.3.3 Same as 5.1.3

5.3.4 Benzene will be measured in the vapor sample and in the solution; a portion of the solution sample is used for this purpose. The remaining portion is analyzed for soluble organics, soluble boron, and selected samples will be analyzed for soluble Cu.

5.3.5 Testing will proceed until sufficient data is gathered to determine decomposition rates of the intermediates.

6.0 Evaluation of Results, Expected Ranges, and Unexpected Results

6.1 Evaluation of results

Evaluation of the test results is one of the most important facets of the test program. Several factors influence and enhance the evaluation process. Analytical uncertainties are quantified by use of matrix blanks and check standards. Historical information on the performance of each analytical method also provides insight into error. Replicate tests are performed to provide data on reproducibility and allow evaluation of the total ("pure") experimental error. Test results are compared to previous tests and plant observations. Data is reviewed, as available, first by the performing organization and then with the requesting organization to determine as early as possible if tests need to be repeated or additional tests are required. Finally, uncertainties in the data are evaluated and documented as part of the reporting process.

6.2 Expected range of results

- TPB Decomposition, Benzene Generation, and Catalyst Activity
  As evidenced by TPB decomposition and benzene generation rates, the catalyst activity determined for the Tk 48H, Batch 1 simulant is expected to be approximately equal to or greater than that observed in Tank 48H when temperature is taken into account. Rate constants for Tank 48H soluble TPB decomposition shown in Reference 7.3 are in the range of 600 to 1100 L/mole•hr at 50 °C.

- Temperature Dependence/Activation Energy (E_a)
  Previous measurements of rates as function of temperature indicate a higher than typical E_a which means that a decrease or increase in temperature has more effect than generally observed. The E_a reported in References 7.1 and 7.3 range from ~ 90 to 140 kJ/mole.

6.3 Unexpected results

Unexpected results could have test, programmatic, and/or process impacts. Examples of unexpected results and potential impacts include:

- <u>Low</u> catalytic activity from the Tk 48H, Batch 1 simulant
  The immediate impact of low catalyst activity would be that tests would have to run longer in order to obtain usable data on decomposition rates. More importantly, though, is the implication that the Tk 48H, Batch 1 simulant does not include the primary catalyst(s) or that it contains a catalyst poison. This would require additional work to identify and test other candidate catalysts and would likely have a substantial impact on the lab test schedule.

- <u>High</u> catalytic activity from the Tk 48H, Batch 1 simulant
  The immediate impact of high catalyst activity might be that test data is missed because decomposition occurs too quickly. This might require repeat tests at higher sampling frequency or at lower temperatures. Other implications are that future process TPB decomposition and benzene generation rates may not be bounded by rates observed in Tank 48H; pre-treatment to remove catalysts (such as sludge solids) may be required.

- Based on data obtained, projected benzene generation significantly <u>lower</u> than observed in Tank 48H
  This result would indicate other significant reaction mechanism(s) exist and would have to be identified and investigated. This would likely produce a program delay while the new chemistry is investigated.

- Based on data obtained, projected benzene generation significantly <u>higher</u> than observed in Tank 48H.
  This would indicate the projections are conservative and bounding resulting in no apparent impact.

- Unable to isolate primary catalyst or catalyst group
  This result would lead to uncertainty as to whether the projected benzene generation source term is bounding for all possible compositions.

- Intermediates catalysts other than soluble Cu
  Additional testing may be required to identify and quantify the effects of other catalysts for intermediates decomposition. This could produce a program delay.

- Temperature dependence/E_a lower than expected
  The primary impact of this result is that reducing operating temperatures will have less effect than expected. And conversely, the benzene generation rates at planned operating temperatures may be higher than expected. This could have programmatic impact on ITP restart.

- Temperature dependence/E_a higher than expected
  This would be a positive result indicating that reducing temperatures will have more benefit than expected and that control of operating temperatures and compositions are less critical than currently envisioned.

7.0 References

7.1 D. D. Walker, et al, *Decomposition of Tetraphenylborate in Tank 48H (U)*, WSRC-TR-96-0113, Rev. 0, May 1996.

7.2 Department of Energy Implementation Plan for DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 96-1 TO THE SECRETARY OF ENERGY, Revision 0, October 1996.

7.3 M. J. Barnes and T. B. Edwards, *Copper Catalyzed Sodium Tetraphenylborate Decomposition Kinetic Studies (U)*, WSRC-TR-96-0351, Rev. 0, November 1996.

7.4 HLE-TTR-97008, Rev. 0, *Soluble TPB Decomposition and Catalysis*, November 1996.

7.5 D. D. Walker and C. A. Nash, *Results from Tank 48H Slurry Decontamination and Decomposition Experiments in Support of ITP Process Verification Testing (U)*, WSRC-TR-96-0190, September 1996.

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

7.7 M. J. Barnes, *Task Technical Plan for Sodium Tetraphenylborate Decomposition Catalyst Identification Studies (U)*, WSRC-RP-96-600, Rev. 0, draft November 1996.

7.8 C. L. Crawford, *Task Technical Plan for Decomposition Studies of Triphenylboron, Diphenylborinic Acid and Phenylboric Acid in Aqueous Alkaline Solutions Containing Copper (U)*, WSRC-RP-96-568, Rev. 0, November 1996.

7.9 Quality Assurance Manual (U), Westinghouse Savannah River Company Procedure Manual 1Q.

7.10 Conduct of Engineering and Technical Support (U), Westinghouse Savannah River Company Procedure Manual E7.

7.11 Savannah River Technology Center Procedures Manual (U), Westinghouse Savannah River Company Procedure Manual L1.

7.12 Analytical Development Section Analytical Operating Procedures (U), Westinghouse Savannah River Company Procedure Manual L16.1,Vol's I to IV.

8.0 Attachments

None.

APPENDIX B:

TEST PLAN FOR STABILITY OF SOLID CESIUM AND POTASSIUM TETRAPHENYLBORATE

DNFSB 96-1 IMPLEMENTATION PLAN COMMITMENT #3, MILESTONE #5.2.2-2

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ADC &
Reviewing
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Name and Title
Date: 1-27-97

1.0 Introduction & Background

The In-Tank Precipitation (ITP) facility at the Savannah River Site initiated radioactive operation in Tank 48H in September of 1995. During pump operation in December of 1995, benzene evolved from Tank 48H at higher rates than expected, though the operational safety limit was never approached. Later investigations revealed the source of benzene was apparently from the catalytic decomposition of excess sodium tetraphenylborate (NaTPB) added to ensure adequate suppression of cesium solubility.[7.1]

In August 1996 the Defense Nuclear Facilities Safety Board (DNFSB) issued Recommendation 96-1. The DNFSB recommended that operating and testing in the ITP facility not proceed without an improved understanding of the mechanisms of benzene generation, retention, and release. In the 96-1 Implementation Plan,[7.2] the Department of Energy developed its approach to resolve the issues raised by the DNFSB. This plan is based on a revised safety strategy that will be developed from a combination of laboratory, pilot scale and plant tests that are aimed at understanding benzene generation, retention, and release. The test program includes these elements:

- Benzene generation
  - + determine catalyst(s), mechanisms, and rate constants for decomposition of soluble TPB^-
  - + study stability of solid CsTPB and KTPB
  - + confirm using actual wastes
- Benzene retention
  - + determine capacity of slurries to retain benzene
  - + endeavor to understand the physical forms in which benzene is retained
- Benzene release
  - + develop an understanding of how benzene is released in lab scale tests and in pilot scale demonstration
  - + determine plant equipment mass transfer coefficients in plant tests

Implementation Plan Commitment # 3 states that an overall bounding benzene generation rate will be determined and documented based on the understanding of all major generation mechanisms. Under Milestone #5.2.2-2, laboratory studies are to be completed to determine if insoluble TPB^- compounds contained in the slurry can decompose at a significant rate under expected process conditions.

Although the preponderance of data indicates that soluble TPB^- chemically decomposes to generate benzene, concern over direct reaction of solids was raised when higher than anticipated levels of soluble ^{137}Cs were observed when a Tank 48H slurry sample was treated with additional NaTPB in earlier laboratory tests.[7.4] Attempts to reproduce the observed result until all the soluble NaTPB was destroyed were incomplete due to limited volumes of test samples. More work is needed to improve the baseline experimental data and determine if the present predictive calculations can adequately explain the observed levels of soluble ^{137}Cs and K^+. This test plan describes the planned studies to determine the factors influencing the observed increase in soluble ^{137}Cs and K^+. Real waste studies under controlled conditions will provide improved baseline information. Simulant studies will be done to improve the understanding of the relative stability of solid KTPB and CsTPB, and to identify factors that influence their decomposition.

2.0 Scope

The scope of this test plan covers activities to be performed by the Environmental Molecular Sciences Laboratory (EMSL) of the Pacific Northwest National Laboratory (PNNL) and the Savannah River Technology Center (SRTC). These activities are related to the stability of the solid phase KTPB and CsTPB and observations related to the observed increase in soluble ^{137}Cs in laboratory and plant tests.[7.6]

The EMSL researchers will evaluate the thermodynamics of potential reactions to determine if solid TPB^- compounds are favored to decompose spontaneously. This evaluation will be based on thermodynamic properties of the reactants and products of the postulated reactions for TPB^- decomposition. Results from this work could eliminate direct chemical reactions (without first dissolving) of solid KTPB and CsTPB as significant, based strictly on thermodynamic arguments.[7.6]

The SRTC researchers will mathematically calculate TPB^- degradation and the rate of increase in ^{137}Cs solubility. These calculations will be based on currently available solubility data,[7.7] kinetic data on chemical degradation of soluble TPB^-, and kinetic data on radiolytic degradation of solid KTPB and CsTPB. Calculated and experimental results will be compared to determine if these data adequately explain the observed rate of increase of soluble ^{137}Cs in plant and laboratory tests.

Using radioactive waste from Tank 48H, SRTC researchers will generate additional data on the increase in soluble ^{137}Cs to supplement currently available results in support of the predictive calculations. The effects of solid KTPB concentration, sodium molarity, excess soluble TPB^- and temperature will be tested directly. Absorbed dose through irradiation of simulants will be used to determine if radiolysis affects chemical degradation of KTPB and CsTPB. Concentrations of degradation products (triphenylboron; sodium salts of diphenylboronic acid, phenylboric acid and phenol) will also be monitored in these tests to gain insight on any effect that they may have on the observed results.[7.6]

Additional tests using non-radioactive simulated waste are planned to provide appropriate correlations and kinetic data to refine the TPB^- degradation calculations. Details of the parameters to be examined in these tests will be finalized after the radioactive waste tests are completed.[7.6]

3.0 Objectives and Expectations

3.1 Objectives: The test objectives are designed to determine if direct chemical decomposition of solid KTPB and CsTPB needs to be considered as a major mechanism for generating benzene in the ITP process. A Technical Task Request (TTR)[7.5] has been issued by ITP Engineering (ITP-E) defining tasks for this plan:

3.1.1 Evaluate thermodynamics of various reactions, including direct reactions of solids, through comparison of free energies (ΔG) of alternative reactions to determine which specific reactions and reaction products are most favored thermodynamically.

3.1.2 Using existing solubility data and kinetics data for chemical degradation of soluble TPB^- and radiolytic degradation of TPB^-, calculate TPB^- degradation to establish if calculations are consistent with the observed increase in soluble ^{137}Cs and K^+ obtained from laboratory tests and plant operations (*i. e.*, 1983 demonstration, 1995-96 data from ITP operations).

3.1.3 Develop reproducible baseline data using radioactive waste to determine the rate of increase in soluble ^{137}Cs and K^+ as the concentration of excess NaTPB approaches zero. To the extent possible, the effects of excess NaTPB, decomposition products, and temperature should be determined. If possible, Late Wash conditions should also be simulated as part of these baseline tests (fully washed, no added NaTPB, 65 °C).

3.1.4 Analyze the improved baseline data (from 3.1.3) to determine if results from this and other tests adequately explain the observed increase in soluble ^{137}Cs and K^+, or if direct chemical decomposition of solid KTPB and CsTPB is occurring.

3.1.5 Using non-radioactive simulants, determine effects of absorbed dose, temperature, concentration of solid phase KTPB, concentration of Na^+, excess K^+, organic decomposition products and sludge solids on the kinetics of solid phase KTPB degradation.

3.1.6 If directed by ITP-E and the ITP Flowsheet Task Team, determine the effect of solid particle size on kinetics of solid phase KTPB degradation.

3.1.7 If requested, provide correlations and rate constants for use in process modeling.

3.2 Expectations: At the conclusion of activities under this plan, it is expected that:

3.2.1 The significance of solid phase KTPB and CsTPB degradation to the overall rate of benzene generation in ITP and Late Wash processes will be established.

3.2.2 Predictive calculations of TPB^- degradation will be developed that includes all significant mechanisms that contribute to the observed increase in the concentration of soluble ^{137}Cs and K^+ in KTPB slurries produced, processed and stored in ITP and Late Wash equipment. NOTE: Solid degradation should not be included in the calculations if this mechanism is negligible when compared to other mechanisms (chemical degradation in solution; radiolytic degradation).

3.2.3 If solid KTPB is found to degrade at a significant rate, when compared to other identified mechanisms, parameters such as sodium concentration and temperature will be varied to ensure predictive calculations are applicable throughout the ITP and Late Wash processes.

3.2.4 If solid phase KTPB degrades at a significant rate, when compared to other identified mechanisms, appropriate correlations for important parameters for any significant reaction(s) will be determined to provide improved understanding of the mechanism.

4.0 Test Methodology and Approach

4.1 Key test parameters must be selected or controlled to produce the expected results. Predictive calculations must be validated and supported by experimental test results.

4.1.1 Temperature is an extremely important parameter since previous testing indicates that observed decomposition of soluble TPB^- is a stronger function of temperature than typical, uncatalyzed chemical reactions. Based on reported activation energies,[7.1,7.3] the TPB^- reaction rate doubles every 4 to 6°C. Selected test temperatures must: (1) be high enough to produce measurable decomposition in a reasonable period of time; (2) span or bound the temperature limits in the safety basis; and (3) provide sufficient information on temperature dependence to evaluate operation at temperatures which produce very low decomposition rates.

Current plans for future ITP operations include safety basis temperature limits of 40 °C and operating limits of 35 °C for all operations except Late Wash. Startup testing indicates Late Wash may operate at temperatures as high as 65 °C unless additional process cooling is provided. Previous work shows tests performed at 50 °C or higher produce reasonably rapid and measurable decomposition of soluble TPB^-. The dependence of the rate constant on temperature will be obtained from the slope and intercept of a plot of reciprocal temperature (1/T(°K)) against the natural log of the rate constant (ln k). The intercept is the pre-exponential factor (a) and the slope is the activation energy (E_a) in the Arrhenius equation:

$$k = a\, e^{-(E_a/RT)}$$

Experiments at three different temperatures are sufficient to ensure a good fit and to allow extrapolation with confidence, especially to lower temperatures where the rates are too slow for practical experiments. Typically, tests at three different temperatures (in the range of 40 to 70 °C) will be used to determine the temperature dependence of rate constants.

4.1.2 Compositions must be selected to ensure relevance to the process and to maximize experimental productivity. Test compositions are selected based on documentation of previous process samples and test objectives. The researchers define and document the experimental compositions in the Task Technical Plan that is reviewed and approved by ITP Engineering and the ITP Flow Sheet Task Team. Appropriate analyses are done during the course of the experiments to determine the actual compositions used in the tests (see Table 1).

4.1.3 Projected conditions to be used in these studies are described in the Task Technical Plan (TTP) prepared in response to the TTR and summarized below (see 4.2).

4.2 Testing for this test plan will be performed under the TTP prepared by the performing organization.[7.6] The thermodynamic evaluation will be done at EMSL. All other tasks will be performed at SRTC. The TTP contains information on methods, temperatures, compositions, test conditions, and analytical requirements. The TTP is summarized below.

4.2.1 Thermodynamic Evaluation of TPB^- Degradation at EMSL

A statement of work has been provided to EMSL describing calculations of the free energy for reactions of both solid phase and aqueous phase TPB^- reactants at 25 °C, which is the reference temperature normally used for thermodynamic properties. This temperature is similar to the expected ITP processing temperature of < 35 °C. The purpose of this work is to determine if the reactions of solid KTPB and CsTPB are thermodynamically favored to occur spontaneously, and whether the thermodynamic driving force for these reactions is significant compared to reaction in solutions. SRTC researchers will coordinate the work under this subcontract.[7.6]

4.2.2 Mathematical Calculations

Additional solubility data for NaTPB, KTPB and CsTPB using conditions and compositions more closely simulating ITP processing have recently been obtained. These solubility data, available data for radiolytic degradation of TPB^- compounds and reaction rate data for chemical degradation of soluble TPB^- will be used to calculate the increase in soluble ^{137}Cs as various reactions occur. Results from these predictive calculations will then be compared to observed laboratory and plant data to establish if the calculations adequately predict the observed rate of increase in soluble ^{137}Cs. Refinements to the model will be done as additional degradation rate data is obtained from this or other related work. [7.1, 7.3, 7.4, 7.7, 7.8]

4.2.3 Tank 48H Slurry Experiments

Tests with Tank 48H radioactive waste will provide data to determine if the solid KTPB concentration affects the overall rate of benzene generation. These tests will also provide data on the rate of increase in ^{137}Cs concentration to compare to projected concentrations from calculations. Only two previous laboratory tests with Tank 48H slurries reacted long enough to consume all of the excess NaTPB. Thus, limited information is available on the behavior of ^{137}Cs after excess NaTPB is destroyed. Additional data is also needed to supplement the currently available results on intermediate decomposition products and gain insight into their possible effect on degradation. Information from these tests will also be used to determine if the calculations described above (see 4.2.2) adequately predict the observed increase in soluble ^{137}Cs and K^+ in both the plant and laboratory tests. As a part of these experiments with radioactive slurry, conditions approximating those expected for Late Wash operations will also be tested. The results of these tests will be used to identify conditions most likely to produce solid TPB decomposition to support subsequent simulant testing.

4.2.4 Simulant Testing

The final parameters and conditions for simulant tests will be determined when the the Tank 48H slurry tests are completed. Currently, the effects of the following parameters on the increase in soluble ^{137}Cs and K^+ and the stability of solid KTPB are proposed to be tested using non-radioactive simulants:

- absorbed radiation dose
- temperature
- concentration of insoluble KTPB
- concentration of Na^+

- excess K^+
- concentration of organic decomposition products
- sludge solids

These experiments will be aimed at understanding factors that influence the decomposition of solid KTPB and CsTPB, if results obtained from radioactive tests in this test plan and other related tests (see Appendix A) indicate that chemical degradation of solid KTPB and CsTPB occurs at a significant rate. Prior to initiating these tests with simulants, results from other tests will be evaluated to establish if other parameters should also be included. For example, agitation is not presently included in the list above, but it may alter the rate of solid KTPB decomposition by increasing interaction between KTPB solids and sludge solids.

4.3 Control of Experimental Conditions

Slurry composition and temperature are the two major experimental variables.

4.3.1 To ensure the compositions of the Tank 48H waste slurries (see 5.1) and simulant slurries (see 5.2) are controlled, composition variables shown in Table 3 will be measured and recorded for all slurries tested.

4.3.2 All experiments will be run at constant temperature.

4.3.3 Temperatures of Tank 48 waste slurries will be measured by a thermometer or thermocouple. Accuracy will either be verified to be within ± 2 °C at 0 °C (ice water bath) and 100 °C (boiling water) or through calibration using other methods traceable to NIST standards.

4.3.4 Thermostatted ovens or baths that can control temperatures to ± 3 °C will be used for tests on simulant slurries. Temperatures in these tests will be measured using thermometers traceable to NIST standards.

TABLE 1

COMPOSITIONAL VARIABLES FOR SLURRIES

Solution Density
Weight Percentage of Insoluble solids
Weight Percentage of Soluble solids
Solution concentrations (soluble species):
    Total Na^+
    Nitrate
    Nitrite
    Free Hydroxide
    TPB^-
    Other organics (3PB, 2PB, 1PB, phenol)
    Cu
    K^+
Inorganic solids content:
    Fe, Al, Si, Ca, Cr, Mg, Mn, Cu, Ti

5.0 Test Descriptions

5.1 Tank 48H Slurry Experiments

5.1.1 Test slurries will be prepared using radioactive waste slurry obtained from Tank 48H. One set of four experiments will be run to test primary effects of temperature, soluble TPB^- concentration, and insoluble KTPB concentration. A second set of two experiments will be run to test the effect of projected Late Wash conditions. The test matrix and approximate starting compositions for these tests are shown in Table 2.

5.1.2 All tests will be done using slurry sealed under an air atmosphere in carbon steel vessels. Periodically, the test slurries will be sampled and each sample will be filtered before analysis. Sampling will begin within a few days after the experiments begin. Sampling frequency will be adjusted based on reaction rate to ensure that all of the slurry is not consumed by sampling before soluble TPB^- from NaTPB has all decomposed. NaTPB will be added to reduce the ^{137}Cs concentration below the limit needed for filtration in ITP and disposal as Saltstone.

5.1.3 The slurries will be placed in clean, sealed vessels and then maintained unstirred in a temperature controlled environment. The temperature will be maintained at a setpoint ± 2 °C except when opening the oven door to obtain periodic samples.

5.1.4 The reaction will be followed by measuring ^{137}Cs, K^+ and soluble organic components (TPB, 3PB, 2PB, 1PB, phenol) in the filtrate obtained from each sample. Initial starting compositions will also be determined by sampling, filtering and analyzing after NaTPB has been added to the slurry.

5.1.5 After all sample results are obtained, results will be evaluated to determine if all key parameters for additional tests using simulants (see 5.2 below) have been identified prior to beginning tests with simulants. Predictive calculations using solubility, soluble reaction rates and radiolysis will also be compared to results to determine if chemical degradation of solids is indicated to be significant.

TABLE 2
RADIOACTIVE WASTE TEST DESIGN

Set 1: Tank 48H Tests (initial $[Na^+]$ ~ 3.5 M)

Run #	Temp. (°C)	Initial $[TPB^-]$ (mg/L)	Initial [KTPB] (wt %)
1	40	100	1
2	40	400	4
3	50	400	1
4	50	100	4

Set 2: Late Wash Tests

Run #	Temp. (°C)	Initial $[TPB^-]$ (mg/L)	Initial [KTPB] (wt %)	Initial $[Na^+]$ (M)
1	65	400	4	0.5
2	65	400	4	1.5

5.2 Simulant Testing

Simulant tests will be used to establish correlations and rate constants for solid phase KTPB degradation. Non-radioactive tests can be done more rapidly, at less expense, and without radiation exposure to personnel. Testing with simulants will be done in two parts.

5.2.1 A simulated slurry will be prepared and tested at the same conditions as one of the radioactive waste tests described in Section 5.1. This test is necessary to demonstrate that simulant responds similarly to the radioactive Tank 48H slurry.

5.2.2 After simulant tests are shown to be representative of the radioactive tests, a statistically designed set of tests will be completed. The main effects of key parameters identified as part of the evaluation of radioactive tests will be tested. In addition, 2-factor interactions between several of the parameters will be tested.

5.2.3 The design of these experiments will be optimized based on considerations listed in Table 3. If other important parameters are identified in the radioactive waste tests, the scope of the simulant tests will be expanded. Based on the initial test design outlined in Table 3, about 36 tests will be performed in 3 blocks. The effect of all parameters will be included in the first block of tests and 2-factor interactions will be tested in the other two blocks.

5.2.4 All tests will be done using about 100 milliliters of slurry sealed under an air atmosphere in carbon steel vessels. Periodically, the test slurries will be sampled and each sample will be filtered before analysis. Sampling will begin within a few days after the experiments begin. Sampling frequency will be adjusted based on reaction rate to ensure that all of the slurry is not consumed before all of the soluble TPB^- from excess NaTPB addition has decomposed.

5.2.5 The slurries will be placed in clean, sealed vessels and then maintained unstirred in a temperature controlled environment. The temperature will be maintained at the specified setpoint ± 2 °C except when slurries are removed from the oven or water bath for sampling.

5.2.6 For tests using simulants, reactions will be followed by analyzing for TPB^- and soluble K^+ in the filtrate obtained from each sample as the reaction proceeds. Initial starting compositions will also be determined by sampling, filtering and analysis after NaTPB has been added to the slurry.

5.2.7 After all sample results are obtained, results will be evaluated to provide correlations and reaction rate constants for chemical degradation of solid phase KTPB.

TABLE 3
EXPERIMENTAL FACTORS FOR SIMULANT TESTS

Factor	Low Value	High Value
Temperature	40	65
KTPB, wt%	1	5
$[Na^+]$, M	0.5	5.0
Sludge, wt%	0.1	1.0
Organics*, mg/L	0	900
K^+:TPB^- ratio, mg/L	0:200	25:0
Radiation dose, Mrad	0	100

Design

7-factor, two-levels
36 runs in three blocks
2 centerpoints repeated in each block

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*Organics include equal masses of intermediate degradation products

6.0 Evaluation of Results, Expected Ranges, and Unexpected Results

6.1 Evaluation of results

Evaluation of the experimental results is one of the most important facets of the test program. Several factors influence and enhance the evaluation process. Analytical uncertainties are quantified by use of matrix blanks and check standards. Historical information on the performance of each analytical method also provides insight into error. Replicate tests are to be performed in tests using simulants to provide data on reproducibility and allow evaluation of the total ("pure") experimental error. Test results are compared to results from previous tests and plant observations. For this test plan, use of the experimental data to compare to predictive calculations provides yet another check for internal consistency and reasonableness of the data. Data and calculations are reviewed, as available, first by the performing organization and then with the requesting organization to determine as early as possible if tests need to be repeated or additional tests are required. Finally, uncertainties in the data are evaluated and documented as part of the reporting process.

6.2 Expected range of results

- Thermodynamic Calculations

Theoretical considerations generally show that overcoming the crystal lattice energy is a significant factor in the reactions of solids, especially when compared to homogeneous liquid phase reactions in which species are already dispersed as ions. In an aqueous system containing insoluble ionic solids, the heat of hydration of the ionic components can be a major factor in thermodynamic calculations related to chemical reactions. Because KTPB and CsTPB are lower in solubility compared to NaTPB, ionic hydration energy is less of a factor in thermodynamic considerations for KTPB and CsTPB. Results from these calculations are expected to show the thermodynamically favored reaction products, and provide some insight into the relative stability of intermediate degradation products. Note that consideration of phenomena at the solid-liquid interface would be expected to contribute to the degradation rate of less soluble KTPB and CsTPB in an aqueous slurry. Physical properties such as total surface area, adsorption, and diffusion of interactive species from the surface could play a role in observed rates of TPB^- degradation and benzene generation. These phenomena will not be considered in the thermodynamics calculations. Since the thermodynamic calculations are necessarily incomplete, they will only be used to provide additional insights in the context of the entire test program, not as a final answer.

- Predictive Mathematical Calculations

Historically, calculations for the ITP process based on literature data predict higher ^{137}Cs and K^+ concentrations for a given set of conditions than have been observed experimentally or in plant tests. Solubility data obtained under conditions more closely approximating the composition and conditions actually present in the ITP slurries has recently been obtained. After this solubility data is incorporated, calculated concentrations are expected to agree more closely with those actually observed in plant and laboratory tests. In addition to improved solubility data, calculations of TPB^- degradation are expected to incorporate all major degradation mechanisms. A contribution from solid phase chemical degradation of KTPB and CsTPB is not presently included in predictive calculations. These would be included in future calculations only if this postulated mechanism is found to be significant compared to other identified mechanisms.

- Tank 48H Slurry Experiments

  These tests are expected to provide improved baseline data to test the calculations that are done to predict the overall TPB^- degradation observed in ITP. If this baseline data indicates KTPB and CsTPB solids are degrading through direct chemical reaction at a significant rate, this data would be used to develop preliminary chemical reaction rate constants for their chemical decomposition. These rate constants would then be used in the calculations of TPB^- degradation.

- Simulant Tests

  If evaluation of experimental data indicate direct chemical reaction of KTPB and CsTPB is occurring at a significant rate, then correlations for parameters that could affect decomposition of solid KTPB and CsTPB are expected to be developed to aid the understanding of the decomposition. Appropriate kinetic expressions and rate constants are expected to be developed to improve the accuracy of predictive calculations.

6.3 Unexpected results

The preponderance of data indicates that the principal mechanisms of TPB^- degradation have been identified, and KTPB and CsTPB do not rapidly decompose under process conditions and storage in ITP. However, if the increase in soluble ^{137}Cs and K^+ observed in plant and laboratory tests cannot be adequately explained, then more work will be needed to clearly identify other mechanisms and determine their effect on the process. Unexpected results could have test, programmatic, and/or process impacts. Examples of unexpected results and potential impacts include the following:

- If solid KTPB is not relatively stable, projected benzene generation by this mechanism could be significantly <u>higher</u> than that observed from other mechanisms.

  This result would indicate the projections for long-term storage stability are not conservative and bounding, since the KTPB solids are a significant potential source of benzene. Such a result would require major effort to resolve the potential consequences.

- Calculations using the best available solubility and kinetic data predict soluble ^{137}Cs and K^+ increases at a <u>faster</u> rate than that observed in the plant.

  This result would show the current calculations based on solubility considerations, chemical degradation of soluble TPB^- and radiolytic degradation does not include all significant mechanisms that affect ^{137}Cs and K^+ solubilities. For example, adsorption of NaTPB on the surface of the solid KTPB has been postulated to account for lower than expected soluble NaTPB in filtrate, leading to lower than expected ^{137}Cs solubility. Experimental solubility measurements do not account for absorbed TPB^- as being available for reaction in solubility expressions used in calculations. This result would be conservative and bound the expected ranges of operation in the plant.

- Calculations using current solubility and kinetic data (including kinetic data from solid phase KTPB degradation) predict soluble ^{137}Cs and K^+ increases at a <u>slower</u> rate than that observed in the plant.

  This result would indicate that other mechanisms that increase dissolution of ^{137}Cs and K^+ have not yet been incorporated into predictive calculations. This result would not be conservative and could result in a programmatic impact on restart until the other mechanisms are identified.

7.0 References

7.1 D. D. Walker, M. J. Barnes, C. L. Crawford, R. F. Swingle, R. A. Peterson, M. S. Hay and S. D. Fink, *Decomposition of Tetraphenylborate in Tank 48H (U)*, WSRC-TR-96-0113, Rev. 0, May 10, 1996.

7.2 Department of Energy Implementation Plan for DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 96-1 TO THE SECRETARY OF ENERGY, Revision 0, October 1996.

7.3 M. J. Barnes and T. B. Edwards, *Copper Catalyzed Sodium Tetraphenylborate Decomposition Kinetic Studies (U)*, WSRC-TR-96-0351, Rev. 0, November 7, 1996.

7.4 D. D. Walker and C. A. Nash, *Results from Tank 48H Slurry Decontamination and Decomposition Experiments in Support of ITP Process Verification Testing (U)*, WSRC-TR-96-0190, September 1996.

7.5 HLE-TTR-97015, Rev. 0, *TPB Solids Stability*, November 1996.

7.6 M. J. Barnes, R. A. Peterson and D. D. Walker, *Technical Task Plan for Solids Stability Studies of Tetraphenylborate Slurries (U)*, WSRC-RP-96-602, Rev. 0, December 9, 1996.

7.7 D. J. McCabe, *Cesium, Potassium, and Sodium Tetraphenylborate Solubility in Salt Solution (U)*, WSRC-TR-0384, Rev. 0, December 16, 1996.

7.8 D. D. Walker, *Benzene Distribution in Product Streams from In-Tank Processing (U)*, DPST-86-390, January 15, 1987.

7.9 R. A. Jacobs, *DNFSB 96-1 Implementation Plan - Commitment #3, Milestone #5.2.2-1 - Test Plan for Catalytic Decomposition of Soluble Tetraphenylborate*, HLW-DBA-96-0028, December 18, 1996.

8.0 Attachments

None.

97/270

APPENDIX C:

TEST PLAN FOR BENZENE RETENTION MECHANISMS AND CAPACITIES

DNFSB 96-1 IMPLEMENTATION PLAN COMMITMENT #5, MILESTONES #5.2.3-1 & #5.2.3-2

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1.0 Introduction & Background

The In-Tank Precipitation (ITP) facility at the Savannah River Site initiated radioactive operation in Tank 48H in September 1995. During pump operation in December 1995, benzene evolved from Tank 48H at higher rates than expected, though the operational safety limit was never approached. Subsequent investigations revealed the source of benzene was catalytic decomposition of excess, soluble tetraphenylborate (TPB) that was added to assure adequate suppression of cesium solubility.[7.1]

In August, 1996 the Defense Nuclear Facilities Safety Board (DNFSB) issued Recommendation 96-1 in which the Board recommended operation and testing not proceed without an improved understanding of the mechanisms of benzene generation, retention, and release. In the 96-1 Implementation Plan,[7.2] the Department of Energy developed its approach to resolve the issues raised by the DNFSB. The plan is based on the development of a revised safety strategy and a combination of bench, pilot scale and plant tests aimed at understanding benzene generation, retention, and release. Further, the test program includes these elements:

- Benzene generation
  - \+ determine catalyst(s), mechanisms, and rate constants for decomposition of soluble TPB
  - \+ study stability of solid CsTPB and KTPB
  - \+ confirm using actual wastes

- Benzene retention
  - \+ determine capacity of slurries to retain benzene
  - \+ endeavor to understand the physical forms in which benzene is retained

- Benzene release
  - \+ develop an understanding of how benzene is released in lab scale tests and in pilot scale demonstration
  - \+ determine plant equipment mass transfer coefficients in plant tests

Implementation Plan Commitment # 4 states that benzene retention mechanisms and retention rates (capacities) will be determined for ITP waste slurries and filtrate. Commitment #4 contains two related milestones which will both be met under this test plan. Milestone #5.2.3-1 requires a test plan to define the important retention mechanisms while Milestone #5.2.3-2 requires a test plan to determine the capacity and distribution of benzene retention in Tank 48H slurry as a function of controlling parameters. This test plan describes studies to be performed to determine how and how much benzene is retained in TPB slurries above the "apparent solubility" limit (see Appendix D).

2.0 Scope

The scope of this test plan covers activities performed by the Savannah River Technology Center (SRTC). These activities will determine the capacity and distribution of benzene in KTPB slurries above the apparent† solubility limit (see Appendix D) as a function of controlling parameters such as KTPB solids concentration, sodium concentration, agitation/quiescence, temperature, etc. Data and observations from these studies are expected to elucidate how the benzene is retained and the relative releasability of the different retention mechanisms.

Estimates of benzene retained in Tank 48H and observations of bench scale testing show that benzene can be retained in quantities well in excess of that which is soluble in the solution. The retention and slurry-vapor equilibrium of benzene in slurries up to the apparent solubility limit are being studied as described in Appendix D. Scoping tests indicate the apparent solubility limit for a 3 wt % KTPB slurry (5 M Na^+) is about 1800 mg/L.[7.3] However under quiescent conditions in Tank 48H, benzene was observed at much higher concentrations - 7000 to 8000 mg/L.[7.1] In addition, on March 5, 1996 a small quantity of benzene was released at rates much greater than previously observed indicating the possibility of retention by a different mechanism in a more readily-released form.

The studies described in this test plan have been divided into three key elements:

- investigation of methods to detect and observe benzene in KTPB slurries,
- bench scale tests to determine the impact of process variables on benzene retention capacity and release, and
- pilot scale tests to study retention and release on a scale and in equipment that is expected to allow direct and indirect observation of the benzene retention form/mechanism.

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† In a liquid-liquid solution with very limited solubilities such as benzene and water, the equilibrium vapor pressure of benzene above the solution is less than the pure benzene vapor pressure at the same temperature if the solution is not saturated with benzene. When the solution reaches the saturation point (incipient two-phase liquid), the benzene vapor pressure over the solution is equal to the vapor pressure of a pure benzene phase. Up to saturation, the ratio of benzene in the vapor to benzene in the liquid is generally approximately constant and is known as the Henry's Law constant. As previously mentioned, benzene is "soluble" in KTPB slurries at much higher concentrations than for the salt solution alone. Similar to a liquid, as benzene concentration in the slurry increases the equilibrium vapor pressure over the slurry rises approximately linearly until it reaches the vapor pressure of pure benzene. At this concentration, the slurry has become saturated with benzene at the "apparent solubility" limit of benzene.

3.0 Objectives and Expectations

3.1 Objectives: The test objectives seek to provide an understanding of how and where benzene is retained in quantities above the apparent solubility limit, how these quantities are affected by process parameters, and release rates of benzene from the retention forms encountered. A Technical Task Request (TTR)[7.4] has been issued by ITP Engineering (ITP-E) defining the specific tasks for this plan. Stated tasks are:

3.1.1 Under agitated and quiescent conditions, determine benzene retention capacity and releasability as benzene is accumulated beyond the apparent solubility limit. Note: It has been judged that agitation would prevent benzene from accumulating beyond the apparent solubility limit; therefore, tests will be maintained under quiescent conditions until the release tests are performed

3.1.2 Determine the effects of time, [KTPB], temperature (and other significant parameters determined during the "apparent solubility" testing described in Appendix D) on benzene retention beyond apparent solubility.

3.1.3 Continue testing at increasing benzene accumulation until the mass transfer coefficient increases consistent with the benzene release rate observed on March 5, 1996. Note: Mass transfer coefficients will not be determined during this testing; however, baseline release rate measurements and observations are expected to be sufficient to determine if benzene has reached a readily-released form.

3.1.4 During above testing or in experiments specifically for this purpose, use available measurements/observation methods to develop an understanding of the probable mechanisms and physical forms, (*e.g.*, coalesced droplets, rag, free layer) by which benzene is retained beyond the apparent solubility limit .

3.1.5 If benzene is introduced directly, perform testing or evaluation to show the method used to introduce benzene in the above tests produces results comparable to producing *in situ* benzene by chemical reaction. Note: Benzene will be generated *in situ* for these tests. It is planned to add benzene directly to the slurries only if this prerequisite is met and if the *in situ* benzene generation is inadequate to achieve test objectives.

3.2 Expectations: At the conclusion of tests performed under this plan, it is expected that:

3.2.1 The benzene retention capacity above the apparent solubility limit for KTPB slurries will have been determined.

3.2.2 The effects of various process parameters on benzene retention capacity will have been quantified.

3.2.3 Data on the release rates as a function of process parameters will have been developed.

3.2.4 Benzene will have been accumulated in quantities sufficient to observe easily released benzene.

3.2.5 How and where benzene is retained will have been observed by sampling, analysis, and observation techniques such as optical microscopy, UV microscopy, and/or magnetic resonance imaging.

4.0 Test Methodology and Approach

4.1 Three Task Technical Plans (TTP) control the work related to this test plan. The first,[7.5] covers selection of methods to detect and observe benzene in KTPB slurries. The other two control the bench-scale and pilot-scale tests, respectively.[7.6,7.7] Key parameters for the bench-scale and pilot-scale tests must be selected and controlled to produce the expected results. In both the bench-scale and pilot-scale tests, key parameters specified are the slurry composition, temperature, time, benzene generation technique and rate, and purge rate during quiescent and agitated periods. Additional key parameters in the bench-scale tests are wt % KTPB, wt % insoluble solids, irradiation, and [Na^+]. Variation in particle size would also likely affect results; however, prior work indicates it is difficult to obtain significant changes in particle size.

4.1.1 The slurry composition is a key variable in both bench-scale and pilot-scale tests. It is important the slurry be prepared as specified in the test matrix. In the pilot-scale tests, weight percent KTPB will be varied to determine the effect on benzene retention and release. Insoluble solids will be varied in proportion to the wt % KTPB. The [Na^+] will be maintained at 4.7 M with the exception of two tests where it will be diluted during the release testing. In the bench-scale tests, wt % KTPB, wt % insoluble solids, and [Na^+] will be varied to determine their effect on benzene retention and release. After preparation, slurry samples will be submitted to provide data on starting composition.

4.1.2 Several responses are affected by temperature: benzene generation rate, solubility, and vapor pressure. Temperatures will be controlled to assure that temperature variability does not affect the results.

4.1.3 In these tests, quiescent time is a principal parameter. Release tests and other required operations will be performed at the time intervals specified in the test matrix.

4.1.4 The technique for introducing benzene could have significant impact on the results. To ensure the most reliable results, benzene will be generated *in situ* in these tests at a rate comparable to that in Tank 48H (see Section 3.1.5 of this appendix). It is thought this technique is necessary to produce the benzene retention mechanisms encountered in Tank 48H.

4.1.5 N_2 purge will be maintained to simulate the conditions of Tank 48H. The purge will be set to provide a turnover rate comparable to Tank 48H but will be increased during the release testing to provide sufficient flow to obtain good release rate measurements.

4.1.6 Irradiation causes a significant change in the slurry rheology.[7.8] Radiation is postulated to damage the particle surface and change it from very hydrophobic to less hydrophobic. If so, irradiation may have a significant impact on benzene retention. Limited tests will determine if this effect is significant; based on the results of these tests, additional tests may be needed.

4.1.7 Significant variation in KTPB particle size, and thus the surface area, would be likely to have a significant effect on the benzene retention capacity. However, studies by Swingle and Walker show that particle size is only slightly affected by precipitation time and sequence.[7.9] The time to combine the salt and NaTPB solutions was varied from rapid to almost six days. Also, the standard sequence (adding NaTPB to salt solution which results in all the precipitation occuring at very low KTPB solubility) was compared to reverse addition (adding salt solution to NaTPB which starts the precipitation at relatively higher KTPB solubility). Nevertheless, consistent particle size in these tests will be assured by preparing each slurry using a standard procedure. An attempt will be made to measure particle size using a Coulter counter or a scanning electron microscope.

4.2 Testing for this plan will be performed under the TTPs prepared by the performing organization.[7.6,7.7] The TTPs contain detailed information on methods, temperatures, compositions, test conditions, and analytical requirements. The general methodologies for both the bench-scale and pilot-scale tests are similar and are summarized below.

4.2.1 Prepare slurry, establish purge, maintain at 40 °C, sample liquid and vapor.

4.2.2 Maintain quiescent and observe, sample vapor, raise to test temperature after four days.

4.2.3 Maintain quiescent, maintain purge and temperature, observe, sample vapor and liquid at specified frequency, monitor and videotape as needed or as specified in test matrix.

4.2.4 At the end of the quiescent period, sample as specified, increase purge, agitate, monitor release rate, sample slurry when homogeneous, turn off agitation and reduce purge to normal after 30 minutes.

4.2.5 After seven more days, repeat release tests and continue until benzene is deinventoried (pilot-scale) or less than 50% of peak (bench-scale).

5.0 Test Description

5.1 Elements common to both bench-scale and pilot scale tests

5.1.1 The slurry composition will be based on the 4 wt % KTPB formulation devised for testing at the University of South Carolina.[7,10] The recipe will be adjusted as needed to produce slurries at other specified solids concentrations. This formulation has been tested and shown capable of producing *in situ* benzene.

5.1.2 Two baseline tests will be performed to determine release rates from aqueous solutions. The first will use a water/benzene solution with benzene added until it exceeds the solubility limit. This will baseline the release rate for "readily-released" benzene. The second will be from an aqueous solution well below saturation and will baseline the release rate for benzene which is not readily releasable. In a third baseline test, benzene will be added to a slurry beyond the "apparent solubility."

5.1.3 During the quiescent period, the vessels will be purged with N_2 at a rate to produce a headspace turnover rate of about 2-3 hours (similar to Tank 48H). During the release test period, the purge rate will be increased sufficient to ensure the gas phase does not limit mass transfer and to provide good release rate measurements.

5.1.4 Tests will have a nominal duration of either 30 or 60 days. This should be sufficient to produce benzene accumulation equal to or greater than observed in Tank 48H.

5.1.5 With the exception of one pair of tests in bench-scale series, the nominal temperature maintained through the quiescent period will be 50 °C and will be controlled within ± 3 °C. The temperature may be increased if necessary to increase the benzene generation rate.

5.2 Bench-scale tests

5.2.1 A total of twenty tests are planned in the bench-scale studies. These tests are designed to study the effects of controlled parameters on benzene retention and release for slurries above the apparent solubility and will cover the range of conditions expected in ITP and Late Wash.

5.2.2 Tests will be conducted in sealed 2 liter glass vessels maintained at constant temperature by either a constant temperature bath or by a water jacket. The vessels will be equipped with agitators, ports for nitrogen purge inlet and outlet, and a port for liquid sampling.

5.2.3 For the nominal quiescent periods of 30 or 60 days (Q = 30 or 60), the planned test sequence is:

Day 1: Establish N2 purge (2-3 hours holdup time); agitate as required for slurry makeup; ramp temperature to 40 °C by end of day

Days 2-6: No agitation, maintain 40 °C; sample liquid and vapor every other day, vapor first; analyze for benzene

Day 6: Ramp to specified temperature

Days 6 to Q-1: Maintain specified temperature; sample liquid and vapor weekly for benzene; at day Q-1, also analyze liquid sample for TPB decomposition products

Day Q: Maintain specified temperature; increase purge; prepare for on-line vapor sampling; agitate slurry; sample/analyze vapor at the maximum rate capable by analytical device; continue for 30 minutes; stop agitation and return to quiescent conditions

Day Q+7: Repeat agitation and release test until release rate is < 50% of peak rate observed on day Q.

5.2.4 Test Matrix

5.2.4.1 The first six tests will be a factorial test of the effects of slurry concentration (1 to 12 wt % KTPB) and time (30 to 60 days).

5.2.4.2 The remaining sixteen tests will vary a single parameter to determine if the parameter has a significant effect: insoluble solids, absorbed radiation dose, salt composition (*i.e.*, ionic strength), temperature and Na^+ concentration. Some tests will be conducted at a low enough slurry concentration to ensure the effect is not overwhelmed by the slurry itself; others will be performed at slurry concentrations expected during washed precipitate storage and in Late Wash.

5.3 Pilot-scale tests

5.3.1 A total of nine tests comprise the pilot-scale studies. These tests are designed to provide a demonstration which will determine where/how benzene is retained in the slurry and when/how the benzene becomes readily releasable from the slurry to the vapor phase.

5.3.2 Tests will be conducted in transparent glass columns to allow visual observations of slurry and benzene phases. The vessels will be about 7.5 in ID and about 6 ft tall. They will be equipped with numerous sample ports along the length of the column. The vessel lid will include ports for N_2 purge inlet and outlet, agitator bearing and shaft, thermocouples, heat transfer coil inlet and outlet, and vapor sample. The temperature will be maintained with the heat transfer coil using hot water.

5.3.3 During release testing, agitation will be provided by a pump circulating from the bottom of the column to one of several discharge ports located along the column length. If necessary, agitation can be adjusted by moving the discharge port closer to, or farther from, the floating slurry. Circulation rate could be adjusted and/or the agitator could be operated.

5.3.4 For the nominal quiescent periods of 30 or 60 days (Q = 30 or 60), the planned test sequence is:

Day 1: Establish N2 purge (2-3 hours holdup time); add chemicals and agitate for slurry makeup; ramp temperature to 40 °C by end of day; analyze vapor for benzene and liquid for benzene and soluble TPB

Days 2-5: No agitation, maintain 40 °C; inspect slurry daily; analyze vapor for benzene

Day 6: Ramp to specified temperature; analyze vapor for benzene; inspect column contents

Day 7: Photograph, videotape, and sample at selected locations along column length; analyze vapor for benzene and analyze liquid for benzene and soluble TPB

Days 7 to Q-1: Maintain specified temperature and low purge rate; maintain weekly vapor benzene analysis; maintain weekly photographing, videotaping, and liquid analyses for benzene and soluble TPB

Day Q: Maintain specified temperature; photograph, videotape, and sample along entire column length; analyzer vapor for benzene and liquid for soluble TPB and TPB decomposition products; increase purge; prepare for on-line vapor benzene analysis; start pump to mix slurry; sample slurry when column contents are homogenized; sample/analyze vapor at maximum rate capable by analytical device; continue agitation for 30 minutes; reduce N_2 and reestablish quiescent conditions; photograph, videotape, and sample at selected locations along entire column length

Day Q+n*7 (for n = 1, 2, 3, ...): Repeat agitation, vapor sampling, quiescent sequence under high N_2 purge rate for n cycles until peak benzene concentrations differ by no more than 5 %, time permitting;

determine time to de-inventory slurry of benzene; continue release testing to deplete benzene from slurry; photograph, videotape, and sample along entire column length

5.3.5 Based on observations and data collected during testing, selected samples will also be characterized to determine the physical nature of the retained benzene using the methods developed to detect and observe benzene in KTPB slurries.[7.5] One criterion for selecting samples for such characterization is release rate.

5.3.6 Test Matrix

5.2.6.1 The first six tests will test the effect of slurry concentration at three different concentrations and the effect of time, 30 and 60 days, on benzene retention and release.

5.2.6.2 The next two tests will examine how benzene is released while diluting the salt solution sufficiently to cause the slurry to sink. The quiescent period will be 30 and 60 days.

5.2.6.3 The ninth test will last for up to 120 days in an effort to form a separate benzene layer. If a separate layer is formed, the material will be monitored for benzene release. An intentional release test will be performed only after obtaining sufficient data on release under quiescent conditions.

6.0 Evaluation of Results, Expected Ranges, and Unexpected Results

6.1 Evaluation of results

Evaluation of the test results is one of the most important facets of the test program. Several factors influence and enhance the evaluation process. Analytical uncertainties are quantified by use of matrix blanks and check standards. Historical information on the performance of analytical methods also provides insight into the error. Test results are compared to previous tests and plant observations. Data is reviewed, as available, first by the performing organization and then with the requesting organization to determine as early as possible if tests need to be repeated or additional tests are required. Finally, uncertainties in the data are evaluated and documented as part of the reporting process.

6.2 Expected range of results

- Retention capacity
  The amount of retained benzene is expected to range from as low as a few thousand mg/L average (or lower) to as high as 10,000 mg/L average by complete decomposition of the 0.03 M excess NaTPB. 10,000 mg/L at 1 wt %

KTPB could be equivalent to as high as 100,000 mg/L in a 10 wt % KTPB slurry in terms of retention and releasability.

- Release rates
  The observed release rates should fall within the range of rates established in the baseline tests. Along with visual and enhanced observation methods, the baseline test with benzene above the solubility limit and the comparison of release rates are expected to provide the bases for determining if "readily released" benzene has been formed.

- Observed or inferred retention mechanisms
  The observed or inferred retention mechanisms may range from simple aqueous solubility and surface adsorption on TPB solids to the formation of a free benzene layer.

6.3 Unexpected results

Unexpected results could have test, programmatic, and/or process impacts. Examples of unexpected results and potential impacts include:

- Low benzene generation
  In situ benzene generation rates may be lower than expected. Rates will be monitored by liquid and vapor sampling during the quiescent period. The test temperature could be increased if necessary to increase the TPB decomposition rate. If increasing the temperature is ineffective, there would be an adverse schedule impact. Other options for increasing benzene include increased catalyst, increased NaTPB, or direct benzene addition if confirmed to be an adequate method of introduction.

- Relative release rates which do not correspond to rates observed in Tank 48H
  Release rates are expected to be an indication of controlling mass transfer from the slurry to the vapor. As such, release rates from slurries with high benzene retention should be relatively higher than from low benzene retention and should correspond in a predictable way to mass transfer rates observed during Tank 48H pump operations and depletion runs. Lack of correspondence would likely indicate some systematic inadequacy in the test methodology and would likely result in significant programmatic delay.

- Inconsistent results
  Poor consistency might be caused by factors such as inconsistent *in situ* benzene generation rates, the combination of particle size effect (surface area) and particle size variability, or other inadequately understood or controlled experimental factors. The potential impact would depend on the magnitude of the inconsistency and would range from calculational uncertainty (requiring more conservative assumptions and operating conditions) to additional, revised experiments.

- Significant effects from insoluble solids, irradiation, decomposition intermediates, or surfactants
  These parameters are not currently included in the retention test matrices because it is judged they are unlikely to have a significant effect. They are, however, included in the apparent solubility tests (Appendix D) and can be added to these tests if necesary.

7.0 References

7.1 D. D. Walker, *et al.*, *Decomposition of Tetraphenylborate in Tank 48H (U)*, WSRC-TR-96-0113, Rev. 0, May 1996.

7.2 Department of Energy Implementation Plan for DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 96-1 TO THE SECRETARY OF ENERGY, Revision 0, October 1996.

7.3 R. A. Peterson, C. L. Crawford, and R. F. Swingle, *Initial Estimates of Mass Transfer Coefficients in Tank 48H and Tank 50H (U)*, SRT-LWP-96-256, August 1996.

7.4 HLE-TTR-97018, Rev. 0, *Benzene Retention and Release from KTPB Slurries Beyond Apparent Solubility (U)*, November 15, 1996.

7.5 L. O. Dworjanyn, *Task Technical Plan for Detection of Benzene in ITP Slurries (U)*, WSRC-RP-96-627, January 1997.

7.6 W. B. Van Pelt, *Task Technical Plan for In-Tank Precipitation Benzene Retention Bench-scale Tests (U)*, WSRC-RP-97-11, Rev. 0, January 1997.

7.7 J. C. Marek, *Task Technical Plan for Pilot-Scale Benzene Retention and Release Demonstration (U)*, WSRC-RP-97-7, Rev. 0, January 1997.

7.8 D. D. Walker and J. P. Doherty, *The Effect of Gamma Irradiation on the Rheology of KTPB Slurries (U)*, DPST-88-926, November 1985.

7.9 R. F. Swingle and D. D. Walker, *Initial Results of In-Tank Precipitation Reverse Cycle Addition Tests (U)*, WSRC-RP-94-1285, Rev. 0, December 1994.

7.10 C. A. Nash and R. A. Peterson, *Test Outline for the Filter Research Unit/ITP Support at the University of South Carolina*, SRT-LWP-96-0087, Rev. 3, December 1996.

8.0 Attachments

None.

APPENDIX D:

TEST PLAN FOR LABORATORY BENZENE RELEASE STUDIES

DNFSB 96-1 IMPLEMENTATION PLAN
COMMITMENT #5, MILESTONE #5.2.4-1

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Date: 1-27-97

1.0 Introduction & Background

The In-Tank Precipitation (ITP) facility at the Savannah River Site initiated radioactive operation in Tank 48H in September 1995. During pump operation in December 1995, benzene evolved from Tank 48H at higher rates than expected, though the operational safety limit was never approached. Subsequent investigations revealed the source of benzene was catalytic decomposition of excess, soluble tetraphenylborate (TPB) that was added to assure adequate suppression of cesium solubility.[7.1]

In August, 1996 the Defense Nuclear Facilities Safety Board (DNFSB) issued Recommendation 96-1 in which the Board recommended operation and testing not proceed without an improved understanding of the mechanisms of benzene generation, retention, and release. In the 96-1 Implementation Plan,[7.2] the Department of Energy developed its approach to resolve the issues raised by the DNFSB. The plan is based on the development of a revised safety strategy and a combination of bench, pilot scale and plant tests aimed at understanding benzene generation, retention, and release. Further, the test program includes these elements:

- Benzene generation
  - + determine catalyst(s), mechanisms, and rate constants for decomposition of soluble TPB
  - + study stability of solid CsTPB and KTPB
  - + confirm using actual wastes

- Benzene retention
  - + determine capacity of slurries to retain benzene
  - + endeavor to understand the physical forms in which benzene is retained

- Benzene release
  - + develop an understanding of how benzene is released in lab scale tests and in pilot scale demonstration
  - + determine plant equipment mass transfer coefficients in plant tests

Implementation Plan Commitment # 5 states that tests will be conducted and plant data evaluated to quantify benzene release rates for both planned and inadvertant plant evolutions. Benzene release calculations require a quantitative understanding of how much benzene is retained in the slurry and the slurry-vapor equilibrium (SVE) at varying conditions. Milestone #5.2.4-1 requires a test plan for laboratory release studies to be issued January 1997. This test plan describes studies to be performed on potassium tetraphenylborate (KTPB) slurries to determine slurry benzene retention capacities and benzene SVE relationships.

2.0 Scope

The scope of this test plan covers activities performed by the Savannah River Technology Center (SRTC). These activities will determine slurry benzene retention capacities and benzene SVE relationships for KTPB slurries under varying conditions up to the "apparent solubility" limit for benzene in the slurry.[†]

Walker reported vapor-liquid information for benzene in simulated salt solutions which quantified the effects of high ionic strength salt solutions on the vapor pressure of benzene.[7.3] Walker also reported some preliminary results in earlier studies that TPB slurries reduced the vapor pressure of benzene as compared to the salt solution and that the solubility of benzene in the slurry was higher than in the salt solution alone.[7.4] Observations of benzene generation and release in Tank 48H, Batch 1 indicated very high benzene retention and recent studies by Crawford provided additional data confirming this behavior.[7.5]

To perform calculations on the benzene release rate from the slurry, the rate at which benzene is generated, how much is retained in the slurry (retention capacity), and how benzene is released must be quantitatively understood. One of the factors controlling release rate is the benzene vapor concentration at the liquid-vapor interface which can be expressed as the product of the liquid (slurry) benzene concentration and the SVE ratio (analogous to Henry's Law constant). This test plans describes studies to determine the benzene solubility (retention) and the SVE relationship at varying conditions for TPB slurries containing benzene up to the maximum"apparent solubility. "

Tests are described in this test plan to determine the apparent solubility and the SVE relationships for KTPB slurries as a function of temperature, salt solution composition and concentration, absorbed radiation dose, decomposition intermediates and surfactant concentrations. Monosodium titante (MST), sludge solids or aqueous specific gravity will also be tested to determine if they have significant effect.

At times, the observed quantities of benzene retained in Tank 48H, Batch 1 were well in excess of preliminary values reported for apparent solubility.[7.6] By definition, the vapor pressure over these systems is equal to the vapor pressure of pure benzene. The benzene retention capacities and relative benzene release rates for these systems will

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[†] In a liquid-liquid solution with very limited solubilities such as benzene and water, the equilibrium vapor pressure of benzene above the solution is less than the pure benzene vapor pressure at the same temperature if the solution is not saturated with benzene. When the solution reaches the saturation point (incipient two-phase liquid), the benzene vapor pressure over the solution is equal to the vapor pressure of a pure benzene phase. Up to saturation, the ratio of benzene in the vapor to benzene in the liquid is generally approximately constant and is known as the Henry's Law constant. As previously mentioned, benzene is "soluble" in KTPB slurries at much higher concentrations than for the salt solution alone. Similar to a liquid, as benzene concentration in the slurry increases the equilibrium vapor pressure over the slurry rises approximately linearly until it reaches the vapor pressure of pure benzene. At this concentration, the slurry has become saturated with benzene at the "apparent solubility" limit of benzene.

be studied under the test plans described for Commitment #4, Implementation Milestones #5.2.3-1 and #5.2.3-2.

Tests to characterize the retention and release of benzene from slurries containing benzene in concentrations above the apparent solubility are discussed in Appendix C.

3.0 Objectives and Expectations

3.1 Objectives: The test objectives are designed to develop benzene retention capacities and SVE ratios for KTPB slurries up to their apparent solubility limits. A Technical Task Request (TTR)[7.7] has been issued by ITP Engineering (ITP-E) defining the specific tasks for this plan. Stated tasks are:

3.1.1 Determine slurry and vapor benzene concentrations and apparent solubility limits for benzene in KTPB slurries as a function of temperature, ionic strength, quantity of KTPB solids, radiation dose greater than 75 Mrads, decomposition intermediates, and surfactants.

3.1.2 Determine if MST, sludge solids, or aqueous specific gravity (*i.e.*, solids floating versus sinking) affect the results and perform additional testing if required.

3.1.3 Provide correlations for use in modeling the flowsheet and for evaluating benzene retention and release.

3.2 Expectations: At the conclusion of tests performed under this plan, it is expected that:

3.2.1 Apparent benzene solubilities will have been determined for slurry compositions and conditions encountered throughout ITP and Late Wash.

3.2.2 SVE ratios, including any significant non-linear behavior with benzene concentration, will have been determined for slurry compositions and conditions expected throughout ITP and Late Wash.

3.2.3 When combined with data produced in other tests, benzene retention and release will be adequately understood and modeled.

4.0 Test Methodology and Approach

4.1 Key parameters must be selected and/or controlled to produce the expected results. As specified in the Task Technical Plan, the key parameters to be controlled and varied are temperature, salt composition and concentration (*i.e.*, ionic strength), TPB solids concentration, concentrations of decomposition intermediates and surfactants, insoluble solids (sludge and MST), irradiation, and specific gravity.[7.8] Slurry particle size, leakage from the test vessels, method of benzene introduction and equilibration time are parameters which may affect the results that will be controlled but not varied.

4.1.1 The high apparent benzene solubility in TPB slurries is believed to be primarily due to association with the solids. Consequently, the TPB concentration will range from 1 wt % to 12 wt % to carefully explore the range of expected solids concentrations.

4.1.2 Solubility is a function of temperature; temperatures will span the range of ambient (25 °C) to the expected maximum in Late Wash (65 °C).

4.1.3 Benzene solubility in aqueous solutions ranges from about 1800 ppm in pure water to as little as 100 ppm in 6 M Na^+ solutions.[7.3] This is due to the "salting out" effect at high ionic strength. The salt concentration will range from 5 M Na^+ (ITP) to 0.2 M Na^+ (Late Wash) and will include floating slurry (5 M Na^+) versus non-floating slurry (2.0 M Na^+). As discussed in Fowler's memorandum,[7.9] the influence of ionic strength and resultant activity coefficients can be explored by use of the nominal compositions of average salt, high hydroxide, and high nitrate (low hydroxide).

4.1.4 Soluble organics such the decomposition intermediates (3PB, 2PB, and 1PB) or surface active agents (Surfynol,® tributylphosphate (TBP), and Dow Corning antifoams) may increase the solubility of benzene or affect the proposed adsorption of benzene on the TPB solids. Tests will be performed at maximum expected concentrations to determine if there is any significant effect. If there is a significant effect, additional tests may be warranted.

4.1.5 Though considered unlikely, insoluble solids such as sludge and MST may affect the apparent benzene solubility. Tests will be performed to determine if there is a significant effect; additional tests may be needed.

4.1.6 Irradiation causes a significant change in the slurry rheology.[7.10] Radiation is postulated to damage the particle surface and change it from very hydrophobic to less hydrophobic or even hydrophilic. If so, irradiation may have a significant impact on benzene retention. Limited tests will determine if this effect is significant; additional tests may be needed.

4.1.7 The KTPB particle size, and thus the surface area, is likely to have a significant effect on the benzene retention capacity. However, studies by Swingle and Walker show that particle size is only slightly affected by precipitation time and sequence.[7.11] The time to combine the salt and NaTPB solutions was varied from rapid to almost six days. Also, the standard sequence (adding NaTPB to salt solution which results in all the precipitation occuring at very low KTPB solubility) was compared to reverse addition (adding salt solution to NaTPB which starts the precipitation at relatively higher KTPB solubility).

Nevertheless, consistent particle size in these tests will be assured by preparing each slurry using a standard procedure. An attempt will be made to measure particle size using a Coulter counter or a scanning electron microscope.

4.1.8 Because of the test methodology, as much as 50% of the added benzene may be lost during the experiments. However, this will not affect the results as long as the vapor and slurry are at steady state at the time of sampling.

4.1.9 The benzene introduction method and equilibration time may affect the results. Because the slurry will be stirred for about one day prior to sampling, which Crawford has shown to be more than sufficient time to reach steady state, the introduction method is not believed to be a concern. The introduction method will be performed in the same manner for each test slurry. In addition, the one-day stirring time to reach steady state will be verified during initial testing. (See also Section 6.3 of this appendix.)

4.2 Testing for this test plan will be performed under a Task Technical Plan (TTP) prepared by the performing organization.[7.8] The TTP contains detailed information on methods, temperatures, compositions, test conditions, and analytical requirements. The general methodology is summarized below.

4.2.1 Prepare the slurry according to the test matrix (see Section 5.2.2) and place in test vessel.

4.2.2 Inject benzene via the septum on the test vessel.

4.2.3 Hold at temperature and stir for 24 hours.

4.2.4 Sample the slurry and vapor and analyze for benzene.

4.2.5 Add more benzene via the septum.

4.2.6 Repeat until the apparent solubility limit is exceeded.

5.0 Test Description

5.1 A total of 26 different combinations (see Section 5.2.2) of slurry composition and temperatures will be run as described below. A total of 17 out of the 26 combinations will include replicates to determine the reproducibility of the test method.

5.1.1 KTPB slurries will be prepared with the dissolved salt compositions specified in the TTP. Solids content and additives (*e.g.*, sludge, MST, and TPB) are added according to the Test Sequence matrices shown in the TTP. (Section 5.2.2 summarizes the test sequence matrices.) For the 5 M Na^+ salt slurries, an initial KTPB slurry concentration of 1 wt % will be prepared directly. The slurry will then be concentrated to 12 wt % and the filtrate retained for dilution as required. Slurry aliquots will be taken from the 12 wt % slurries since experience has shown these slurries do not separate into slurry and clear liquid layers.

5.1.2 The prepared slurry will be placed in a test vessel along with a magnetic stir bar and the vessel closed.

5.1.3 A specified quantity of benzene will be injected through a septum in the test vessel.

5.1.4 The vessel will be placed in a constant temperature (± 2 °C) bath on top of a magnetic stirrer and stirred until the slurry and vapor equalize. The vessel will be checked visually to ensure adequate agitation and will be vented periodically during the first few hours to avoid pressurization.

5.1.5 When the vapor and slurry have equilibrated, both the slurry and the vapor will be sampled and analyzed for benzene by gas chromatograph.

5.1.6 Mass and volume during slurry preparation, gravimetric weight percent solids, and possibly particle size measurements by Coulter counter or scanning electron microscopy will be measured.

5.2 Test Sequences and Test Matrix

5.2.1 Test Sequences

Initially, a series of five test matrices (see Table 1) will determine the effect of several parameters on benzene retention and vapor pressure. Test Sequence #1 will study the effect of salt composition and concentration (*i.e.*, ionic strength) while temperature and KTPB solids are maintained at a constant, intermediate value. In Test Sequence #2, the effects of insoluble solids (sludge and MST) will be studied at constant temperature and ionic strength and low and intermediate weight percent KTPB. The effect of radiation (~ 95 Mrads), mid to high KTPB solids, low ionic strength and mid temperature will be studied in Test Sequence #3. Test Sequence #4 will determine if surfactants or decomposition intermediates have a significant effect. Finally, Test Sequence #5, which is a statistically designed matrix, will explore the effects of temperature and weight percent KTPB solids at high Na^+ molarity.

5.2.2 Test Matrix

Table 1

Test Seq. No.	1	2	3	4	5
Seq. Objective	Salt Content	Insoluble Solids	Irradiation	Int's & Surf's	Temp & % TPB
Tests in Seq.	5	5	3	4	9
Temperature	Mid	Mid	Mid	Mid	5 diff temp's
Wt % TPB solids	Mid	Lo, Mid	Mid, Hi	Mid	5 diff wt % TPB
$[Na^+]$	Hi, Mid, Lo	Hi	Lo	Hi	Hi
Salt composition	Avg OH^-, Hi OH^-, Hi NO_3^-	Avg OH^-	Avg OH^-	Avg OH^-	Avg OH^-
Sludge	No	Yes	No	No	No
MST	No	Yes	No	No	No
Irradiated	No	No	Yes	No	No
Intermediates	No	No	No	Yes	No
TBP	No	No	No	Yes	No
Surfynol®	No	No	No	Yes	No
Dow Corning antifoam	No	No	No	Yes	No
Replicates	Yes	Yes	Yes	Yes	Yes

6.0 Evaluation of Results, Expected Ranges, and Unexpected Results

6.1 Evaluation of results

Evaluation of the test results is one of the most important facets of the test program. Several factors influence and enhance the evaluation process. Analytical uncertainties are quantified by use of matrix blanks and check standards. Historical information on the performance of the analytical methods also provides insight into the error. Replicate tests are performed to provide data on reproducibility and allow evaluation of the total ("pure") experimental error. Test results are compared to previous tests and plant observations. Data is reviewed, as available, first by the performing organization and then with the requesting organization to determine as early as possible if tests need to be repeated or additional tests are required. Finally, uncertainties in the data are evaluated and documented as part of the reporting process.

6.2 Expected range of results

- Apparent solubility limits for benzene in slurries
  The solubility limit for benzene in a 5 M Na^+ salt solution is about 180 mg/L. As Na concentration decreases, the benzene solubility increases to about 1800 mg/L. Crawford has seen about 1800 mg/L in a 3 wt % TPB slurry at 5 M Na^+.[7.6] If effect of TPB solids is proportional to concentration, then the apparent solubility for 12 wt % slurry may be about 7000 mg/L.[7.1] Temperature would be expected to increase solubility slightly. It is expected that sludge solids and MST will have little or no effect.

- SVE ratios
  The Henry's Law constant for benzene over a 5 M Na^+ salt solution is about 3.5. As the apparent benzene solubility increases, the SVE ratios (when calculated in the same manner as a Henry's Law constant) will decrease proportionately. Therefore, the SVE ratio at 12 wt % slurry may be about a factor of 40 (*i.e.*, 7000 ÷ 180) lower.

6.3 Unexpected results

Unexpected results could have test, programmatic, and/or process impacts. Examples of unexpected results and potential impacts include:

- Method for introducing benzene is not adequate
  The catalytic decomposition of soluble TPB and the intermediates produces benzene at a molecular level and at a relatively slow rate. The benzene introduction method proposed for these studies injects liquid benzene directly to the slurry in a short period of time. There is a possibility that benzene produced *in situ* at a slow rate will associate with the KTPB solids differently than when benzene is injected as a liquid. If so, this is likely to affect the results. Initial scoping studies will be performed prior to commencement of the above tests in an attempt to determine if this concern is real. (These scoping studies will also determine the agitation required to obtain good mixing at the higher slurry concentrations.) If a different benzene introduction method must be developed, this would likely have a significant programmatic impact.

- High variability, poor reproducibility in the data
  Poor reproducibility might be caused by an inadequate benzene introduction method, the combination of particle size effect (surface area) and particle size variability, or other inadequately understood or controlled experimental factors. The potential impact would depend on the magnitude of the error and would range from calculational uncertainty (requiring more conservative assumptions and operating conditions) to additional, revised experiments.

- Significant effects from insoluble solids, irradiation, decomposition intermediates, or surfactants

The test matrices are designed to determine if these parameters have a significant effect, not to quantify the effect. If any of these are significant, additional tests would be required to quantify the effects.

7.0 References

7.1 D. D. Walker, *et. al.*, *Decomposition of Tetraphenylborate in Tank 48H (U)*, WSRC-TR-96-0113, Rev. 0, May 1996.

7.2 Department of Energy Implementation Plan for DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 96-1 TO THE SECRETARY OF ENERGY, Revision 0, October 1996.

7.3 D. D. Walker, *Vapor Pressure of Benzene, Methanol, and Isopropanol Over Salt Solutions (U)*, DPST-88-661, March 1989.

7.4 D. D. Walker, *Vapor Pressure of Benzene Over Irradiated Tetraphenylborate Slurries (U)*, DPST-86-646, August 1986.

7.5 C. L. Crawford, Lab Notebook WSRC-NB-95-308, pg. 65-83.

7.6 R. A. Peterson, C. L. Crawford, and R. F. Swingle, *Initial Estimates of Mass Transfer Coefficients in Tank 48H and Tank 50H (U)*, SRT-LWP-96-256, August 1996.

7.7 HLE-TTR-97017, Rev. 0, *Apparent Benzene Solubility and VLE in KTPB Slurry*, November 15, 1996.

7.8 R. F. Swingle, *Task Technical Plan to Study the Effects of Solids on the Apparent Solubility of Benzene in Simulated Salt Solutions (U)*, WSRC-RP-96-775, Rev. 0, December 1996.

7.9 J. R. Fowler and R. A. Jacobs, *Projected Variation in Feeds to the In-Tank Precipitation Process (U)*, OPS-DTZ-97-0004, January 1997.

7.10 D. D. Walker and J. P. Doherty, *The Effect of Gamma Irradiation on the Rheology of KTPB Slurries (U)*, DPST-88-926, November 1985.

7.11 R. F. Swingle and D. D. Walker, *Initial Results of In-Tank Precipitation Reverse Cycle Addition Tests (U)*, WSRC-RP-94-1285, Rev. 0, December 1994.

8.0 Attachments

None.