96-0004338

The Secretary of Energy
Washington, DC 20585

November 12, 1996

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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:

This letter forwards the Department's implementation plan for addressing the issues raised in the Defense Nuclear Facilities Safety Board's Recommendation 96-1.

The implementation plan presents a comprehensive strategy to resolve the safety issues related to the benzene generation at the In-Tank Precipitation Facility. The implementation plan addresses three major areas of investigation regarding the chemical and physical mechanisms of benzene generation, retention, and release. The consolidation and evaluation of the specific laboratory tests will provide the information necessary to revise the Authorization Basis and indicate any modifications needed to resume full operation of the facility.

The implementation plan was prepared by Mr. Lee Watkins, Assistant Manager for High Level Waste, Savannah River Operations Office, in coordination with senior Department managers and Defense Nuclear Facilities Safety Board staff. We appreciate your staff's dedication and support of the development of this plan.

Sincerely,

Hazel R O'Leary

Hazel R. O'Leary

Enclosure

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Department of Energy Implementation Plan

for

DEFENSE NUCLEAR FACILITIES SAFETY BOARD
RECOMMENDATION 96-1 TO THE SECRETARY OF ENERGY
pursuant to 42 U.S.C. § 2286a(a)(5)
Atomic Energy Act of 1954, as amended

In-Tank Precipitation Facility at the Savannah River Site

October, 1996

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Appendices

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 Board). 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 Board 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 anomalous experiment where TPB solids were postulated to rapidly decompose; and
- affirmation of or modification to ongoing improvements to the facility design.

The Board recommended that in-plant testing involving significant quantities of TPB and/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 and 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 and metal hydroxides 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 reviewed and finalized once a better understanding of the following three TPB chemistry issues has been developed,

- The scientific understanding of the reactions leading to the generation of benzene in the ITP Facility will be adequately understood to ensure that defense-in-depth 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 adequately understood to ensure that defense-in-depth 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 adequately understood to ensure that defense-in-depth measures to prevent and/or mitigate deflagration are adequate.

These programs will proceed in parallel as implemented by a dedicated team for each program and a dedicated senior manager for the overall effort.

Critical baseline assumptions involve funding, personnel and laboratory resources. It is also assumed that the basic precipitation process will not be substantially changed.

1.0 BACKGROUND

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 that can be vitrified with radioactive sludge; and a high volume, low activity stream that can be solidified as grout and disposed of as low level waste.

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 that is then filtered. The filtrate is 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 to be combined with radioactive sludge and vitrified.

The ITP process was demonstrated at Savannah River in 1983. The demonstration facility consisted of a 1.3 million gallon high level waste tank (the current ITP processing tank - Tank 48) retrofitted with chemical addition facilities, slurry pumps, process feed pumps, filters, filtrate hold tanks, and process monitoring instrumentation. The actual demonstration was considered to be "full scale" in that a 500,000 gallon batch of radioactive salt solution was chemically treated and filtered producing 450,000 gallons of decontaminated filtrate and 53,000 gallons of 10 wt % precipitate. The precipitate was then washed to reduce the sodium concentration. The demonstration was considered a success and design of the permanent ITP facility started in 1985.

During the demonstration, the amount of benzene released during the precipitate washing step was greater than anticipated. This was the subject of further study at Savannah River and at the University of Florida from 1983 to 1986. The conclusion of the studies was that benzene generated by radiolytic decay of the TPB was retained within the TPB crystal until the addition of water during the precipitate washing step. It was believed that the TPB crystal was dissolved during water addition thus rapidly releasing "trapped" benzene present within the crystal lattice. The permanent ITP facility was designed on this basis.

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 a test plan that 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). A water addition was made without an expected 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. 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 operational safety requirement 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. 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 Justification for Continued Operation was revised to credit nitrogen inerting and to provide less restrictive pump operating limits.

On March 5, 1996, one slurry pump was operated at low (600 rpm) speed. A large quantity of benzene was immediately seen in the tank vapor space and pump operation was terminated after 14 minutes. This data indicates 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, an estimated 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 since that time.

Savannah River had planned to proceed with a series of Process Verification Tests (PVTs) in Tank 48 designed to increase the level of understanding of NaTPB chemistry and release mechanisms. The tests were to proceed after installation of a backup nitrogen supply as part of a program to transition from fuel control to oxygen control as the primary means of assuring safe operation of the ITP Facility. The first such test, PVT-1, would require addition of a small amount of NaTPB to reprecipitate soluble cesium before filter operation and filter cleaning operations were conducted. Key objectives of this test include: determination of the effectiveness of cesium recovery, validation of benzene generation in Tank 48, validation of the benzene generation rate in Tank 50, and to determine the impact of oxalic acid addition to Tank 48. The next test, PVT-2, included significant quantities of new waste and NaTPB to be added to Tank 48. The Department has deferred the conduct of PVT-2 until such time as an improved understanding of NaTPB chemistry is achieved and the appropriate modifications to facility hardware, engineered controls and administrative controls have been completed.

2.0 UNDERLYING CAUSES

The safety issues associated with the ITP process derive from the decomposition of the organic compound sodium tetraphenylborate (NaTPB) into benzene which poses a deflagration hazard in the ITP tanks. The ITP process calls for the addition of NaTPB in excess of that which is stoiciometrically required to precipitate cesium and potassium as TPB solids. Excess NaTPB is used to ensure the necessary cesium decontamination factor is achieved.

The unexpected rapid decomposition of the excess NaTPB observed in Tank 48 was not explained by existing process calculations that were based on radiolytic decomposition and the release of "trapped" benzene during the washing step. The decomposition and release due to these mechanisms was found to be small and lower than expected.

The ITP process was developed through a combination of laboratory scale testing and a full scale demonstration in 1983. As described in Section 1.0, unanticipated benzene release rates observed in the wash step during the 1983 demonstration prompted additional studies at the University of Florida. Based on these studies, it was concluded that benzene generated from radiolysis was trapped in the TPB crystal and was rapidly released during the wash step where large quantities of water are added to the process.

This work had proceeded based on the premises that radiolytic breakdown of TPB was the dominant means of benzene generation and that water addition to TPB crystals containing trapped benzene was the dominant means of release. The University of Florida testing provided an incomplete set of data which was consistent with observed data from the 1983 demonstration, however, the approach did not include a systematic evaluation of all potential contributors to benzene generation, retention and release.

ITP began operation September 25, 1995 on this basis in parallel with ongoing studies at Georgia Tech related to trapped benzene. Washing operations were restricted in the authorization basis pending resolution of the benzene generation and release rates associated with trapped benzene. Initial operations were conducted under a Radioactive Operations Commissioning Test Plan to collect data and validate benzene generation and release rates.

Since depleting the bulk benzene inventory in Tank 48 in April, 1996, an integrated engineering approach has been applied to the development of the testing and chemistry program defined in this Plan. The chemistry program will systematically evaluate 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 will be 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 ITP operations.

This approach provides confidence that safe operations can resume at ITP with appropriate controls and engineered systems in place which have been derived from a reasonable and conservative understanding of mechanisms related to benzene generation, retention and release.

3.0 BASELINE ASSUMPTIONS

Baseline Assumptions are listed below. These are confined to significant events that could divert funding or key personnel away from implementation of this Plan or events that could significantly delay implementation.

Safety Issue Resolution
The conduct of planned testing and research programs will not identify new concerns that significantly change the scope or schedule as defined in this Plan. It is also assumed that the testing and chemistry program results will provide the level of understanding necessary to develop an adequate safety strategy for ITP operations.

Personnel
Personnel considered in the resource loaded schedule will remain available throughout FY97 to develop and complete this program and not subject to reduction in force, outsourcing, downsizing, re-engineering, etc.

Analytical Facilities
Analytical laboratory facilities, including clean and radioactive facilities, will remain functional and available as needed during FY97. Prolonged downtime will not occur due incidents, accidents, failure of critical infrastructure, etc.

Funding
Savannah River funding considered in the resource loaded schedule will be available per the FY97 Annual Operating Plan and that funding will not be rescinded or directed into other programs during the course of FY97.

Plant Configuration
The basic precipitation process will be preserved. An acceptable authorization basis and operating envelope can be developed for the basic process configuration of the ITP facility.

4.0 SUMMARY OF COMPLETED AND NEAR-TERM ACTIONS

The Department has completed several actions with the objective of ensuring the safe condition of the ITP facility until an adequate understanding of tetraphenylborate chemistry is developed and modifications to the facility are complete. Some radioactive testing involving small additions of NaTPB will continue, however; significant additions of NaTPB and/or radioactive waste will not be initiated until an appropriate authorization basis is developed and the necessary engineered features and administrative controls have been determined and implemented in accordance with this Plan.

Following the unexpected benzene release from Tank 48 (see Section 1.0), a systematic program of tank sampling and laboratory testing was begun to understand the underlying chemistry. A detailed report of these studies was issued on May 10, 1996 (reference 10). 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 NaTPB solids in the tank, but no significant amount of insoluble potassium and cesium tetraphenylborate had reacted.

- Benzene was the major product of the decomposition. Phenol and biphenyl are minor products, and phenylboronic acid is 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 10).

- 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.

- The presence or absence of oxygen changes the decomposition mechanism. At elevated temperatures in the absence of oxygen, the reaction initiates instantaneously with benzene as the nearly exclusive product. In the presence of oxygen, benzene is a significant decomposition product, but larger quantities of phenol are formed.

- Under the limited range of reaction conditions tested to date, little difference in stability is observed between Aromatic Flavors and Fragrances, Boulder Scientific, and reagent grade NaTPB. Spray-drying or similar treatments appear to generate limited amounts (<1%) of decomposition products that increase initial benzene generation, but this does not appear to significantly affect the rapid decomposition reaction.

- The release rate of benzene, once it has been formed, is accelerated by the operation of mixing pumps and is readily reduced when the mixing pumps (or other means of agitation) are shut down. The delayed release indicates that benzene is being retained in the precipitate slurry.

PVT-1 Shielded Cells Demonstrations
As part of the preparation for PVT-1, laboratory experiments with high level waste slurries from Tank 48 were conducted in the SRTC Shielded Cells Facility. The results of the PVT-1 demonstrations (reference 15) led to the following conclusions:

- Addition of as little as 0.0003 molar (100 mg/L) excess NaTPB to the slurry in Tank 48 is sufficient to reduce Cs-137 concentrations below 10 nCi/g. This radioactivity level is well below the current and proposed limits in the ITP process requirements.
- Efficient decontamination was achieved using TPB from either Tank 49, Aromatic Flavors and Fragrances, or Holley Oak Chemicals. Thus, earlier concerns that a constituent in Tank 49 could be the cause of the decomposition were not substantiated by these tests.
- There is no evidence that organic decomposition products in Tank 48 prevent acceptable decontamination as long as excess NaTPB is present.
- The excess NaTPB will be at risk of decomposing. The rate of the decomposition reaction increases significantly with temperature between 40 and 50°C. All of the small scale tests indicate that excess NaTPB will degrade slowly if the tank temperature is kept below 40°C. Two tests have shown faster TPB decomposition rates, but inadequate temperature and catalyst concentration controls are the suspected causes. The first of these two tests is referred to as the "anomalous experiment" while the other is often referred to as the "restart test" where significant excess NaTPB was added. The extent of this postulated decomposition is small, and has not exceeded 0.5% of the solids.

Mass Transfer Coefficient Determination
A portion of the ITP plant data collected during the pump runs described in Section 1.0 was used to calculate mass transfer coefficients for Tanks 48 and 50. The remaining data was used to verify the calculations under a variety of process conditions (reference 14). These mass transfer coefficients can be combined with other physical property data and benzene generation rates to determine the amount of benzene in the vapor phase (see Section 5.2.4). The calculation assumes a well mixed vapor and liquid space, and can be applied to Tanks 48, 49, 50, and Late Wash.

PVT-1 Preparations
As described above, flowsheet demonstrations with Tank 48 slurry and predictions of benzene releases have been completed. A Test Plan and procedures have been developed and are in the approval process. The ITP facility equipment is ready. Laboratory readiness to receive the samples from PVT-1 is being completed.

The underlying causes of retention and release have been postulated but are not adequately defined. A chemistry program has been initiated to establish the underlying causes of soluble TPB rapid decomposition, benzene retention and release. The chemistry program will also address the anomalous experiment where TPB solids were postulated to decompose at an unexpectedly high rate. This program is described in Section 5.2 of this Plan.

5.0 SAFETY ISSUE RESOLUTION

5.1 Board Recommendation

The Board believes that the uncertainty in understanding of the science of NaTPB chemistry would make it imprudent to proceed with waste processing without substantial improvement in the level of understanding. Some such improvement may follow from the results of PVT-1. Better understanding of the anomalous experiment suggesting decomposition of TPB solids is also required.

The Board therefore recommends:

1. Conduct of the planned test PVT-2 should not proceed without improved understanding of the mechanisms of formation of the benzene that it will generate, and the amount and rate of release that may be encountered for that benzene.
2. The additional investigative effort should include further work to (a) uncover the reason for the apparent decomposition of precipitated TPB in the anomalous experiment, (b) identify the important catalysts that will be encountered in the course of ITP, and develop quantitative understanding of the action of these catalysts, (c) establish, convincingly, the chemical and physical mechanisms that determined how and to what extent benzene is retained in the waste slurry, why it is released during mixing pump operation, and any additional mechanisms that might lead to rapid release of benzene, and (d) affirm the adequacy of existing safety measures or devise such as may be needed.

A copy of the recommendation is included as Appendix D.

5.2 Safety Issues

As described in Sections 2.0 and 4.0, the safety issues associated with ITP resulted from the decomposition of TPB. Review of the Board's discussion contained in Recommendation 96-1 indicates that there are four safety issues leading to the two recommendations. Each safety issue is discussed below with the appropriate commitments and milestones.

Underlying Philosophy

The underlying philosophy in this 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 studies will be performed to provide bounding values for the key parameters affecting benzene generation, retention and release. These bounding values will then 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 will also be used to define further activities which will refine the bounding values for benzene generation, retention and release.

The studies and experiments to refine the generation, retention and release values will be performed in parallel with the authorization basis modifications. As information is obtained, it will be evaluated as part of the authorization basis development task to ensure that:

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

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

The programmatic risk that results obtained late in this process will indicate that the bounding values are not truly bounding is small. The potential time savings associated with the parallel approach justifies the risk. In the unlikely event that the assumptions are shown to be non-conservative, operations will be delayed until the authorization basis and facility design reflect the refined values.

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 and to use this information 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. It is the Department's goal to incorporate defense-in-depth preventive and mitigative features throughout the hardware design and administrative controls of the ITP facility such that the safety class engineered features are required only during accident or abnormal conditions. Safety structures, systems, and components will be designed for a high degree of reliability.

The PSM Rule, 29 CFR 1910.119, as well as DOE Order 5480.23 discuss the difference between the concepts of "preventive" and "mitigative". For accident scenarios involving toxic or radioactive materials, the preferred method of control is to prevent the accident from occurring, as this protects all populations and minimizes the consequences (usually the consequences are zero). Mitigation is an important level of safety, but should be used only as a last line of defense.

The preventive function includes containment of the hazard, control and protection. Containment of the hazard includes those administrative features which assure the integrity of the containment, such as operator training, preventive/predictive maintenance, inspection, and testing. Control of process upsets which can lead to accidents is achieved through design of automatic or manual control systems and includes defense-in-depth through the use of redundancy. Protection against deviations beyond design or operating limits is accomplished through the use of alarms, interlocks, relief devices, ignition source control, and operator intervention. Mitigative systems or controls reduce the severity of consequences after an accident occurs, but may be designed to limit the source term available during the accident.

Resolution of the ITP safety basis will address both preventive and mitigative functions. Examples of potential safety controls and systems for prevention and/or mitigation of deflagration events are as follows:

> The preventive function can include the establishment of primary inerting control and monitoring of oxygen concentration in the vapor space; establishment of appropriate interlocks to isolate and pressurize the tanks; tank ventilation systems to remove hydrogen and benzene vapors; monitoring for flammable vapor concentrations in the vapor space and operator actions to deenergize pumps; and minimization of spark sources internal to the tank vapor space.
>
> The mitigative functions may include limits on fuel and oxygen concentrations to reduce the energy of a potential deflagration in the tank vapor space thus limiting the entrainment and release of waste to the environment; qualification of the tank integrity under certain deflagration conditions; limits on the curie content and benzene concentrations in the tanks to reduce the source terms available for release; installation of monitoring (oxygen, benzene, and radioactive material) to warn of releases or dangerous concentrations; and emergency response actions to mitigate the doses to onsite and facility workers.

The classification of these or other controls identified during resolution of the chemistry issues or update of the safety analysis have not been determined. This classification will follow the safety philosophy of prevention first, mitigation last, where the primary barrier becomes the first line of defense and subsequent lines of defense are added to protect the barrier from unacceptable events. Mitigative barriers will be added as a means of protecting assumptions such as fuel or oxygen concentrations, source terms, and response to accidents. These barriers will be classified based on their importance relative to the preventive barriers. It is anticipated that many of the preventive and mitigative barriers will not be classified as safety class or safety significant, but that they will be controlled and maintained as part of the defense-in-depth philosophy. This meets the intent of DOE Order 5480.23 and 29 CFR 1910.119.

The program to develop a revised authorization basis is supported by a series of tests using simulated waste to determine the generation, retention and release mechanisms under a series of bounding conditions such as catalyst concentration and temperature. The design of experiments will consider both statistical and single variable designs. These 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.

It is expected that the results of the accident analysis will indicate oxygen control to be a robust preventive strategy and that the preventive safety features at ITP will therefore be driven towards robust tank monitoring, control and inerting systems. The chemistry program will be used to define the most robust approach to fuel control to use as part of the defense-in-depth safety strategy. One of the primary assumptions which must be supported to confirm the adequacy of any ITP safety strategy is that of a well mixed vapor space. Testing in Tank 48 during the first production batch clearly showed that the oxygen level in the vapor space remained uniformly low despite known air ingress to the tank. Additional instrumentation was positioned in the tank vapor space including inside tank risers where the air inleakage was known to occur. This data will be evaluated to determine if additional plant testing is necessary. Benzene concentrations in the vapor space were shown in previous tests to be nearly uniform. The March 5, 1996 tests indicated a horizontal or vertical non-uniformity for a period of a few minutes when a mixing pump was energized after the tank was dormant for nearly three months. Improved understanding of benzene retention and release are expected to explain this phenomenon such that controls and/or engineered systems can be developed, if needed, to prevent or reduce this localized high benzene concentration.

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. This logic process is further described in Appendix G. The leading candidate for a defensible primary safety strategy is one of oxygen control, with redundancy being provided in the form of safety class backup nitrogen systems and tank isolation/pressurization. Fuel control is being pursued as part of the overall defense-in-depth safety strategy for normal operations and as an initial condition for accident scenarios. The chemistry program can be used to ensure adequate understanding exists to provide the means for controlling the generation and release rates and to place the process in a safe configuration for air-based ventilation operation such as can be expected during major maintenance. Modifications to equipment or administrative controls in support of fuel control will be evaluated as the results of the chemistry work are obtained. Revisions to the functional classification and authorization basis will also be accomplished at this time. The Department is also evaluating a positive pressure oxygen control safety philosophy which could eliminate vapor space mixing and air ingress concerns during normal operations. The results of data evaluation and testing will support the selection of the primary safety strategy.

The program will be conducted using the contractor's existing procedures. These require the generation of: 1) Technical Task Requests which provide the scope of the testing and the acceptance criteria; 2) a Task Technical Plan which provides the details of how the testing will be conducted; 3) Task QA Plans which describe the appropriate QA attributes and their controls (see further discussion in Section 6.3); and 4) reports which describe the results of task completion.

5.2.1 Controls and Engineered Systems

Issue Statement

A better understanding of chemistry issues related to ITP must be developed to determine the combination of controls and engineered systems necessary to prevent and/or mitigate benzene deflagration in process vessels.

Resolution Approach

The authorization basis for safe operation of the ITP facility has transitioned from fuel control to oxygen control. The previous safety strategy is being revisited in light of problems encountered in understanding the mechanisms for benzene generation, retention and release and how these mechanisms impact facility safety for all modes of operation and under abnormal and accident conditions. The path forward involves identifying and reviewing potential strategies for safe operation and recommending a safety strategy which will provide the flexibility of operation while maintaining the safety of both offsite and onsite personnel. This effort will consider impacts on normal operations, maintenance, emergency response, environmental compliance, and occupational safety and health. Each strategy will be evaluated in light of existing and new chemistry information, from both a preventive and mitigative aspect, and a final strategy chosen. The evaluation criteria will include the areas of inherent safety, reliability, chemistry impact, maintainability, operability, schedule and cost. The engineering features and administrative controls to implement this strategy will then be determined with respect to the information obtained from sufficient understanding of the process chemistry. The goal of this program is to ensure that an oxygen based authorization basis is well defined and understood. The program will consider both negative and positive pressure operation. Previous studies on vapor space mixing, the potential for pockets of higher oxygen concentration, and the potential for plumes of higher benzene concentration will be reviewed. Additional tests will be defined and performed as required to support selection of the primary safety strategy (see Milestone #5.2.1-2).

Previous attempts to define a fuel control safety strategy for the ITP Facility were based upon an inadequate understanding of mechanisms and rates governing the generation, retention and release of benzene. Sections 5.2.2, 5.2.3, and 5.2.4., describe the series of tests which will be used to further develop the Department's understanding of these mechanisms and rates. Because large releases of benzene could result in challenges to the systems put in place to prevent deflagration, defense-in-depth will be provided through a combination of administrative controls, operating limits, and additional engineered systems which limit the generation, retention and release of benzene.

Prevention and mitigation measures credited for facility safety will meet the goals/targets listed below:

- Safety Systems (structures, systems and components that are relied upon to perform a passive or active function) will be identified in order to ensure safety of the public, worker and protection of the environment.
- Operating Limits (limits on process variables, system setpoints, or other operational parameters) will be developed in order to ensure safety of the public, worker and protection of the environment.
- Administrative Controls (provisions relating to procedures, organization and management, and other administrative measures) will be developed to ensure safety of the public, worker and protection of the environment.
- The facility's authorization basis will be revised to reflect measures relied upon to perform prevention and mitigation functions.
- Prevention and mitigation measures will consider all modes of operation, under both normal and accident conditions, as defined in the facility's authorization basis.
- Safety measures derived from the test results should minimize the impact on facility operations. Additional tests (above those described in Sections 5.2.2, 5.2.3 and 5.2.4) may be considered as necessary to avoid overly restrictive measures.

The focus for understanding the chemistry of ITP operations necessary to achieve defense-in-depth controls on flammable gases will be toward those aspects which will bound the issues of benzene generation, retention, and release. This understanding will be sufficient to identify adequate engineering and administrative controls for maintaining the vapor spaces below the CLFL for benzene/hydrogen mixtures for all but the most severe accident conditions, while minimizing the impact on operations which support ultimate vitrification and filtrate disposal. Defense-in-depth preventive and mitigative features will be incorporated throughout the hardware design and administrative controls of the ITP facility such that the safety class engineered features are required only during accident or abnormal conditions. In addition, the impact of the generation, retention, and release of benzene on controls necessary to support the final safety strategy for operation must be determined. To this extent, the chemistry tasks must accomplish the following milestones to support various aspects of the authorization basis revision:

> 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 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 understood to determine those operations, conditions, and events which can lead to planned and/or inadvertent benzene release. The bounding retention capacity of precipitate slurries must be understood to define the inventory of benzene available for release during worst case operating conditions (e.g., time between pump runs) and for worst case maintenance 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 liquid must be achieved. Improved knowledge of benzene retention mechanisms will support and focus the effort to establish release mechanisms.
>
> Benzene Release: The release rate of benzene vapor is necessary to define time of operation and speed of slurry pumps to safely deplete the precipitate of liquid 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 to bound the benzene release rate from bounding liquid/solids concentrations, from pump operations, worst case releases from a liquid benzene layer, and due to seismic vibration must be obtained. This is to include the effect of temperature and liquid/chemical additions on the release rate.

The relationship of applicable chemistry milestones to completion of the SAR/OSR upgrade program is identified in Appendix G.

Commitment #1

Calculations documenting bounding benzene generation, retention and release values will be performed and documented in a report.

Milestone #5.2.1-1	Complete calculations documenting bounding benzene generation, retention and release
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverables:	Report describing the outcome of the chemistry program confirming or refining the bounding benzene generation, retention and release values
Due Date:	December 1997

Commitment #2

The primary and defense-in-depth administrative controls, operating limits and engineered systems will be finalized and documented.

Milestone #5.2.1-2	Select the primary safety strategy
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverables:	A report which summarizes the basis for selection of the primary safety strategy including discussions on oxygen or fuel control and negative or positive pressure ventilation systems
Due Date:	January 1997

Milestone #5.2.1-3	Finalize the primary and defense-in-depth administrative controls, operating limits and engineered systems
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverables:	A final report which defines the controls and engineered systems necessary to prevent and mitigate deflagration, based on conclusions of the chemistry program
Due Date:	December 1997

5.2.2 Scientific Understanding of Benzene Generation

Issue Statement

The scientific understanding of the reactions leading to the generation of benzene is not adequately understood to ensure that defense-in-depth measures to prevent deflagration are adequate.

Resolution Approach

As described in Section 1.0, the precipitation of Cs-137 uses an excess of sodium tetraphenylborate (NaTPB). Excess NaTPB is both soluble and solid while the KTPB and CsTPB are largely present as solids (precipitate). Soluble TPB species, and to a much lesser extent solid TPB, will undergo decomposition based on results to date (reference

10). Research to date has investigated several potential decomposition mechanisms including radiolysis, thermal breakdown, mechanical destruction, acidic reactions and catalysis.

Radiolysis

Since the conceptualization of the ITP process, TPB is known to decompose from radiolysis. The single molecular bond connecting the phenyl ring to the boron atom is broken by gamma radiation thus forming benzene. Upon formation, free benzene can dissolve in the aqueous phase and evaporate into the vapor phase.

In addition to free benzene, "trapped" benzene (based on work following the 1983 demonstration) was thought to be a major source of benzene. Trapped benzene is produced by radiation damage to excess NaTPB in the tank. The excess present as solid NaTPB receives a large radiation dose during precipitation and production steps in the ITP process. As a solid, ions damaged by radiation are locked in the TPB crystal lattice. During the precipitate washing step, water is added which dissolves the excess NaTPB and releases the trapped benzene where it can then transfer to the tank vapor space.

The research and testing conducted as a part of the facility design bases and since September, 1995, resulted in a good understanding of this mechanism and the contribution of benzene generation from this source is adequately understood (reference 1, 2, 3, 4).

Hydrogen is also produced from the radiolysis of water. This process is well understood and documented (reference 4). Both hydrogen and benzene are flammable gases and contribute to the total available fuel available for combustion. The authorization basis will consider the production of both hydrogen and benzene in the development of the preventive and mitigative features.

Thermal Breakdown

The phenyl ring/boron bond can also be broken by the addition of thermal energy. NaTPB is manufactured in a hydroxide solution environment and then dried for long-term storage. The thermal breakdown issue, in the absence of catalysis, was studied during the vendor development of the drying process. This is adequately understood and documented (reference 5). Benzene generation from this source is encompassed by the benzene generation rate resulting from catalysis.

Mechanical Destruction

Breaking of the molecular bonds by mechanical energy has been postulated. This mechanism was discussed and researched after excess benzene generation was observed in 1995. Laboratory tests using a 1200 rpm mixing pump and an ultrasonic bath indicates that mechanical effects do not increase benzene generation when compared to control tests at the same temperature (reference 6). Plant data in 1995 and early 1996 confirm this conclusion, therefore, benzene generation by this mechanism is considered to be insignificant.

Acidic Reactions

The addition of acid(s) is known to result in the destruction of TPB. This is the basis of the Defense Waste Processing Facility Salt Processing Cell technology. 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 slower than the neutralization reaction). Calculations have been completed which indicate tank mixing is adequate to ensure rapid neutralization. PVT-1 includes a full scale filter cleaning operation as described above. Test data will be obtained to determine the effect of the addition on benzene generation. Test data will be reviewed to determine if additional laboratory or plant data is required (reference 7).

This source of benzene is additive to the sources described above and will be included in the total benzene generation rate considered by the authorization basis.

Catalytic Decomposition

Catalytic decomposition of soluble and potentially solid TPB species has not been as thoroughly researched as the other decomposition mechanisms and needs further understanding. Therefore, catalytic mechanisms will be the focus of resolving this safety issue. Issue resolution is focused in two areas: soluble TPB decomposition and solid TPB decomposition.

Synergistic Effects

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. As an example, the use of pre-irradiated simulants is one approach to uncover synergistic effects involving radiolysis. However, specific tests in this area cannot be prescribed until the interim results of testing on catalytic decomposition of soluble TPB have been evaluated.

To quantify the impact of soluble TPB decomposition on benzene generation, the following test program will be conducted:

1. Tests will be conducted to determine the minimum NaTPB needed to support effective waste processing in order to minimize benzene generation. The effect of temperature, K/Cs ratio, and NaTPB concentration will be considered in the test plan development. The intent of the testing is to identify the minimum excess TPB required to obtain the desired filtrate Cs concentration. Minimizing the excess TPB minimizes the soluble TPB available for decomposition which results in minimum benzene generation and minimize benzene inventory. Minimizing the excess NaTPB in the ITP process may require improved K analysis, improved sampling techniques, or a new approach of incremental NaTPB additions.

2. Tests using simulated waste will be conducted which systematically eliminate/introduce potential catalysts until the significant species are identified. Test planning will consider addition versus removal of catalyst as well as the grouping of the catalysts. Testing will also consider the effect of temperature, atmosphere composition (air, nitrogen, 5% oxygen) and atmosphere dynamics (stagnant versus flowing), container type and size, and mixing.

   The intent is to identify the significant catalyst(s) which result in benzene generation. A potential list of catalysts has been derived from reviews of tank farm historical waste composition records, review of essential material procurement records since site startup, the waste tank characterization program (sample analysis), flow sheet material balances (with respect to recycle or concentration effects for decomposition), observed behavior in laboratory testing, literature surveys, and expert opinion. The current potential catalyst list includes metals and organic species. Potential catalysts are shown in Appendix E.

3. Tests using simulated waste will be conducted to evaluate controlling parameters and their effect on benzene generation. Testing will consider the effects of hydroxide concentration, temperature, and copper species on generation. Testing will also consider the effect of atmosphere composition (air, nitrogen, 5% oxygen) and catalyst. These tests will be used to determine reaction rate constants for TPB, triphenylborate, diphenylborinic acid, and phenylboronic acid.

4. The controlling parameters identified from the tests described above will then be combined in a "worst case" manner such that tests using simulated waste will result in a "bounding" benzene generation rate. This bounding generation rate will then be included in the vapor release calculation to predict tank vapor benzene concentrations. It will also be used as input to the authorization basis and a design bases generation rate when determining the adequacy of existing or specifying new engineered features and administrative controls.

5. Tests will be conducted using actual radioactive waste to confirm that the benzene generation observed using simulants is bounding. The intent of these tests is to ensure that no unknown or unexpected reaction occurs.

To quantify the impact of postulated solid TPB decomposition on benzene generation, the following test program will be conducted:

1. Tests will be conducted to identify possible causes for solid TPB decomposition. Testing will consider soluble and solid catalyst composition, temperature, catalyst concentration and organic decomposition products.

2. Tests will also be conducted to determine solubility and equilibrium data for Na, K, and Cs TPB. Calculations will then be conducted to identify whether continued slow depletion of TPB solids (to maintain soluble TPB equilibrium) is occurring versus solids decomposition. Decomposition of solids would increase the potential benzene inventory available for release to the vapor phase. This data is needed to ensure that rapid decomposition of the solid TPB does not occur.

The intent of these tests is to identify the conditions under which decomposition of the solid TPB occurs such that administrative controls can be developed and implemented.

Commitment #3

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	Complete laboratory studies on catalytic decomposition of soluble TPB
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverable:	Test Plan for catalytic decomposition of soluble TPB
Due Date:	December 1996
Deliverable:	Final report on catalytic decomposition of soluble TPB
Due Date:	October 1997

Milestone #5.2.2-2	Complete laboratory studies on the decomposition of solid TPB
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverable:	Test Plan for decomposition of solid TPB
Due date:	January 1997
Deliverable:	Report on the decomposition of solid TPB
Due date:	September 1997

Milestone #5.2.2-3	Complete PVT-1 testing
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverable:	Report on PVT-1 testing
Due date:	March 1997

Milestone #5.2.2-4	Complete the radioactive waste confirming studies
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverable:	Test Plan for radioactive waste confirming studies
Due date:	April 1997
Deliverable:	Report on radioactive waste confirming studies
Due date:	September 1997

5.2.3 Scientific Understanding Of Benzene Retention

Issue Statement

The scientific understanding of the mechanisms involved with the retention of benzene in the ITP System is not adequately understood to ensure that defense-in-depth measures to prevent benzene deflagration are adequate.

Resolution Approach

Measurements made during ITP Batch 1 indicate that significant quantities of benzene were retained within the liquid slurry (reference 10). The extent of this retention was several orders of magnitude greater than solubility. The physical and chemical basis for this retention will be characterized in a series of tests with both simulant slurries and simulant filtrate. 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.

Tests will be conducted to define slurry retention capacity and mechanisms. Testing to determine the dominant mechanism(s) will include the introduction of benzene into slurries on a molecular level. Introduction methods will consider organic decomposition, sub-micron sparging and ultrasonics. Slurry retention capacity will be determined both with and without surfactants. The effect of temperature and solids concentration will also be considered in the development of tests.

Liquid Solubility
Measurements of benzene solubility in simulated waste solutions, including NaTPB, have been made (reference 11). 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 both slurry and filtrate 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 will increase benzene retention. With sufficient time, emulsions may coalesce into separate phases. However, systems containing particulates and other organic films inhibit coalescence and will 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 define the conditions for formation of benzene dispersions and emulsions 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 12). 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 organic 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 organic TPB solids may have an affinity to form adherent coatings or droplets on the surface of the solids. Such coatings or droplets may results 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. 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 considered in the development of these tests. Key solids retention mechanisms (adsorption, micelles, etc.) will be identified.

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.

Commitment #4

Benzene retention mechanisms and retention rates will be determined for ITP waste slurries and filtrate.

Milestone #5.2.3-1	Define the important benzene retention mechanisms
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverable:	Test Plan for benzene retention mechanisms
Due Date:	January 1997
Deliverable:	Report on benzene retention mechanisms
Due Date:	September 1997
Milestone #5.2.3-2	Determine the capacity and distribution of benzene retention in Tank 48 slurry as a function of controlling parameters
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverable:	Test Plan for benzene retention capacity
Due Date:	January 1997
Deliverable:	Report on benzene retention capacity
Due Date:	September 1997

5.2.4 Scientific Understanding of Benzene Release

Issue Statement

The scientific understanding of mechanisms involved with the release of benzene in the ITP system is not adequately understood to ensure that defense-in-depth measures to prevent deflagration are adequate.

Resolution Approach

As described in Section 5.2.3, there are several postulated mechanisms for retention of benzene in ITP. It is well known that benzene has low solubility in ITP salt solutions (reference 16). It also has been well established that benzene was retained in Tank 48 slurry during Batch 1 in quantities far in excess of soluble concentrations. 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. While the exact mechanisms for benzene retention are not known, key mechanisms are believed to be solubility, adsorption and droplet retention. Thus, it is necessary to better understand the retention mechanisms and the factors that lead to benzene release to ensure that defense-in-depth measures to prevent deflagration are adequate.

Continued benzene generation without periodic removal (e.g., pump operation) can potentially lead to a benzene layer near the liquid surface. Any disturbance of the liquid surface would lead to benzene release by immediate evaporation. This 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 release mechanism provides information necessary to develop administrative controls and/or engineered features.

The primary factors that could lead to benzene release are diffusion, decrease in benzene solubility, changes in solution specific gravity, liquid additions, 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 10). Thus, diffusion from the slurry is a minor factor in benzene release. Sufficient data are available from 1995-96 ITP plant operations to determine mass transfer coefficients for Tanks 48 and 50 in the unagitated state. This data will be evaluated and documented.

Decrease in Solubility
Benzene solubility will decrease with lower temperatures and increased salt concentrations. Also, presence or absence of surfactants can change the apparent solubility. Studies will be conducted to better quantify the effects of temperature, salt concentration, and surfactant additions on benzene solubility (see Sec. 5.2.3) and those data 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 13). 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.

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 3) 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.

Mechanical Agitation

The fact that mechanical agitation will lead to significant increases in benzene release rates is well established (reference 10). 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 14). Also, mass transfer coefficients were calculated for Tank 50, but limited data for Tank 50 prevented determination of accurate values (reference 14). 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 equilibrium constants. Mass transfer coefficients will also be developed for Tank 49.

The effect of seismic agitation will be evaluated to ensure benzene release by this mechanism is bounded by other more dominant mechanisms.

<u>Commitment</u>

Tests will be conducted and plant data will be evaluated to quantify benzene release rates for both planned and inadvertent plant evolutions.

Milestone #5.2.4-1	Completed laboratory benzene release studies
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverable:	Test Plan for laboratory benzene release studies
Due Date:	January 1997
Deliverable:	Report on laboratory benzene release studies
Due Date:	November 1997

Milestone #5.2.4-2	Define bounding mass transfer coefficients for ITP tanks
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverable:	Report on bounding mass transfer coefficients for ITP tanks
Due Date:	May 1997

Milestone #5.2.4-3	Document benzene release rates due to localized agitation caused by previous water or chemical additions
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverable:	Report on benzene release rates due to liquid additions
Due Date:	November 1997

Milestone #5.2.4-4	Establish bounding benzene release rates that could occur during all planned and inadvertent ITP plant evolutions
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverable:	Report on bounding benzene release rates
Due Date:	November 1997

Milestone #5.2.4-5	Define and document the plant sampling program to confirm laboratory findings
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverable:	Sampling Plan for Tank 48 benzene measurements
Due Date:	June 1997

6.0 ORGANIZATION AND MANAGEMENT

6.1 Change Control

Activities related to gaining a better understanding of benzene generation, retention and release mechanisms may result in the discovery of new information which impacts the schedule and commitments defined in this Plan. Substantive impacts result in fundamental changes to the strategy, scope, or schedule delays of greater than 90 days for completion of a milestone. Non-substantive changes do not result in a change in scope or strategy or delays greater than 90 days. The Department's policy will be to: 1) bring to the Board's attention any changes to this Plan as soon as they are discovered; 2) substantive changes will be provided to the Board via formal revision of this Plan; 3) non-substantive changes (those which do not result in changes to scope, strategy or schedule delays of greater than 90 days) will be provided to the Board through formal correspondence from the Responsible Manager; and 4) all changes will be clearly described including the bases for the changes.

6.2 Reporting

In order to assure that the various Department implementing elements and the Board remain informed as to the implementation status of this Plan, the Department's policy will be to provide periodic (generally bi-monthly) progress briefings. In addition to the bi-monthly briefings, reports will be provided as committed in Section 5.0.

6.3 Quality Assurance

All work performed in support of this Plan will be conducted in compliance with 10CFR830.120 Quality Assurance requirements and the WSRC Quality Assurance (1Q) Manual as required for technical services or information related to the validity of, or modifications to, a technical baseline. This requirement shall apply to all support activities in support of this Plan without regard for the functional classification of the associated structure, system or component.

Laboratory test activities will be conducted under a Quality Assurance Program satisfying the requirements of 10CFR830.120. The overall structure of the program will include definition of specific key tasks, as well as existing procedures, sampling plans, work instructions and records.

The chemistry program will also have expert peer review provided by outside experts that have been involved with the ITP process for the past two years.

Appendix A - Acronyms

AMHLW	Assistant Manager for High Level Waste
CLFL	Composite Lower Flammability Limit
Cs	Cesium
DOE	Department of Energy
DPBA	diphenylborinic acid
FY	fiscal year
hr	hour
ITP	In-Tank Precipitation
JCO	Justification for Continued Operation
K	potassium
kg	kilogram
L	liter
mg	miligram
MOC	Minimum Oxygen to support Combustion
MST	monosodium titinate
Na	Sodium
OSR	Operational Safety Requirement
ppm	parts per million
Pu	Plutonium
PVT	Process Verification Test
QA	Quality Assurance
rpm	revolutions per minute
SAR	Safety Analysis Report
SC	South Carolina
Sr	Strontium
SRTC	Savannah River Technology Center
SRS	Savannah River Site
TPB	tetraphenylborate
WSRC	Westinghouse Savannah River Company

Appendix B - Glossary

anomalous experiment	the one experiment where rapid decomposition of tetraphenylborate solids was observed
batch	an ITP batch consists of waste addition to the ITP reaction vessel (Tank 48) followed by addition of dilution water to adjust the Na molarity to about 5.0, addition of sodium tetraphenylborate and sodium titanate, mixing, waiting for the precipitation and adsorption reactions to go to completion, concentration
cycle	an ITP cycle consists of about three ITP batches followed by a washing step whereby the soluble sodium content of the tetraphenylborate precipitate is reduced by continuous water addition and simultaneous filtration to remove the added water
decomposition products	see intermediates
dispersion	a suspension of solid, liquid or gaseous particles in a solid, liquid or gaseous medium - the usage in this Plan is a suspension of organic liquid particles such as benzene in the liquid waste that is being processed
emulsion	a suspension of small globules of one liquid in a second liquid with which the first liquid will not mix
free layer	a layer of relatively pure benzene in an ITP tank as opposed to a dispersion or emulsion of benzene in liquid waste
intermediates	the decomposition of tetraphenylborate results in the production of intermediate chemical compounds including triphenylborate, diphenylborinic acid, phenylboronic acid, phenol and benzene
micelle	a submicroscopic aggregation of molecules in a larger particle
precipitate	to cause a solid substance to be separated from a solution - sodium tetraphenylborate precipitates cesium and potassium from the liquid waste that is being processed in ITP
precipitate slurry	solid cesium and potassium tetraphenylborate mixed with liquid waste in the ITP process
rag layer	in this Plan, rag layer refers to a benzene emulsion that coalesces and forms a separate layer that also contains other particles and contaminants such that it is not a "free layer" of relatively pure benzene

Appendix B - Glossary

retention	a phenomenon where gaseous benzene is generated in ITP waste and, rather than being released into the vapor space of the tank, it is somehow retained in the liquid waste and later released
tetraphenylborate	an ion consisting of four phenyl rings attached to a boron atom - in ITP, this ion is usually combined with sodium, potassium or cesium
trapped benzene	a theory where benzene generated in the tetraphenylborate crystal by radiolysis was retained, or trapped, in the crystal lattice. Trapped benzene was theoretically released rapidly during water addition which dissolved the tetraphenylborate.
wash	see cycle

Appendix C - Summary of Commitments/Milestones

Commitment #1

Calculations documenting bounding benzene generation, retention and release values will be performed and documented.

Milestone #5.2.1-1	Complete calculations documenting bounding benzene generation, retention and release
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverable:	Report describing bounding benzene generation, retention and release
Due date:	December 1997

Commitment #2

The safety strategy; including the primary and defense-in-depth administrative controls, operating limits and engineered systems; will be finalized and documented.

Milestone #5.2.1-2	Select the primary safety strategy
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverables:	A report which summarizes the basis for the selection of the primary safety strategy including discussions on oxygen or fuel control and negative or positive pressure ventilation systems
Due Date:	January 1997

Milestone #5.2.1-3	Finalize the primary and defense-in-depth administrative controls, operating limits and engineered systems
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverables:	A final report which defines the controls and engineered systems necessary to prevent and mitigate deflagration, based on conclusions of the chemistry program
Due Date:	December 1997

Commitment #3

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	Complete laboratory studies on catalytic decomposition of soluble TPB
Responsible Manager:	AMHLW
Applicable Facilities:	In-Tank Precipitation
Deliverable:	Test Plan for catalytic decomposition of soluble TPB
Due Date:	December 1996
Deliverable:	Report on catalytic decomposition of soluble TPB
Due Date:	October 1997

Appendix C - Summary of Commitments/Milestones

Milestone #5.2.2-2 Complete laboratory studies on the decomposition of solid TPB
Responsible Manager: AMHLW
Applicable Facilities: In-Tank Precipitation
Deliverable: Test Plan for the decomposition of solid TPB
Due date: January 1997
Deliverable: Report on the decomposition of solid TPB
Due date: September 1997

Milestone #5.2.2-3 Complete PVT-1 testing
Responsible Manager: AMHLW
Applicable Facilities: In-Tank Precipitation
Deliverable: Report on PVT-1 testing
Due date: March 1997

Milestone #5.2.2-4 Complete the actual waste confirming studies
Responsible Manager: AMHLW
Applicable Facilities: In-Tank Precipitation
Deliverable: Test Plan for actual waste confirming studies
Due date: April 1997
Deliverable: Report on actual waste confirming studies
Due date: September 1997

Commitment #4

Benzene retention mechanisms and retention rates will be determined for ITP waste slurries and filtrate.

Milestone #5.2.3-1 Define the important benzene retention mechanisms
Responsible Manager: AMHLW
Applicable Facilities: In-Tank Precipitation
Deliverable: Test Plan for benzene retention mechanisms
Due Date: January 1997
Deliverable: Report on benzene retention mechanisms
Due Date: September 1997

Milestone #5.2.3-2 Determine the capacity and distribution of benzene retention in Tank 48 slurry as a function of controlling parameters
Responsible Manager: AMHLW
Applicable Facilities: In-Tank Precipitation
Deliverable: Test Plan for benzene retention capacity
Due Date: January 1997
Deliverable: Report on benzene retention capacity
Due Date: September 1997

Appendix C - Summary of Commitments/Milestones

Commitment #5

Tests will be conducted and plant data will be evaluated to quantify benzene release rates for both planned and inadvertent plant evolutions.

Milestone #5.2.4-1 Complete laboratory benzene release studies
Responsible Manager: AMHLW
Applicable Facilities: In-Tank Precipitation
Deliverable: Test Plan for laboratory benzene release studies
Due Date: January 1997
Deliverable: Report on laboratory benzene release studies
Due Date: November 1997

Milestone #5.2.4-2 Define bounding mass transfer coefficients for ITP tanks
Responsible Manager: AMHLW
Applicable Facilities: In-Tank Precipitation
Deliverable: Report on bounding mass transfer coefficients for ITP tanks
Due Date: May 1997

Milestone #5.2.4-3 Document benzene release rates due to localized agitation caused by previous water or chemical additions
Responsible Manager: AMHLW
Applicable Facilities: In-Tank Precipitation
Deliverable: Report on benzene release rates due to liquid additions
Due Date: November 1997

Milestone #5.2.4-4 Establish bounding benzene release rates that could occur during all planned and inadvertent ITP plant evolutions
Responsible Manager: AMHLW
Applicable Facilities: In-Tank Precipitation
Deliverable: Report on bounding benzene release rates
Due Date: November 1997

Milestone #5.2.4-5 Define and document the plant sampling program to confirm laboratory findings
Responsible Manager: AMHLW
Applicable Facilities: In-Tank Precipitation
Deliverable: Sampling Plan for Tank 48 benzene measurements
Due Date: June 1997

Appendix D - DNFSB Recommendation 96-1

A copy of the original Defense Nuclear Facilities Safety Board Recommendation 96-1 is provided in the next five pages of this Plan. Page numbers have been added.

John T. Conway, Chairman
A.J. Eggenberger, Vice Chairman
John W. Crawford, Jr.
Joseph J. DiNunno
Herbert John Cecil Kouts

DEFENSE NUCLEAR FACILITIES SAFETY BOARD

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

August 14, 1996

The Honorable Hazel R. O'Leary
Secretary of Energy
1000 Independence Avenue, SW
Washington, DC 20585-1000

Dear Secretary O'Leary:

On August 14, 1996, the Defense Nuclear Facilities Safety Board (Board), in accordance with 42 U.S.C. § 2286a(a)(5), unanimously approved Recommendation 96-1 which is enclosed for your consideration. Recommendation 96-1 deals with the In-Tank Precipitation System at the Savannah River Site.

42 U.S.C. § 2286d(a) requires the Board, after receipt by you, to promptly make this recommendation available to the public in the Department of Energy's regional public reading rooms. The Board believes the recommendation contains no information which is classified or otherwise restricted. To the extent this recommendation does not include information restricted by the Department of Energy under the Atomic Energy Act of 1954, 42 U.S.C. §§ 2161-68, as amended, please arrange to have this recommendation promptly placed on file in your regional public reading rooms.

The Board will continue to review these preparations for routine activity in the In-Tank Precipitation System and will seek to ensure that Board actions do not delay this important program any more that may be needed for assurance of safety. Should the Secretary accept the recommendations, the Board is prepared to allocate priority resources in the form of Board members and staff to join in expedited development of a mutually acceptable Implementation Plan.

The Board will publish this recommendation in the Federal Register.

Sincerely,

John T. Conway

John T. Conway
Chairman

Enclosure

c: Mr. Mark B. Whitaker, Jr.

DEFENSE NUCLEAR FACILITIES SAFETY BOARD

RECOMMENDATION 96-1 TO THE SECRETARY OF ENERGY

pursuant to 42 U.S.C. § 2286a(a)(5)
Atomic Energy Act of 1954, as amended.

Dated: August 14, 1996

The Defense Nuclear Facilities Safety Board (Board) has devoted substantial attention to the planned use of the In-Tank Precipitation (ITP) System at the Savannah River Site, because of its importance to removal of high-level radioactive waste from storage tanks at that Site, and because certain unique hazards are associated with the ITP process.

The hazards are a consequence of the volatile and flammable organic compound benzene that is released during the process in amounts that must not exceed safe limits. The benzene is generated through decomposition of tetraphenylborate (TPB) compounds. These compounds are added in the process with the objective to precipitate and remove radioactive cesium from solution in the waste water destined for the saltstone process. The concentrated slurry containing the precipitated cesium constitutes a much smaller volume than the original waste, and its feed to the vitrification process leads to production of a correspondingly smaller amount of glass ultimately to be disposed of in a repository.

The proposed treatment process calls for addition of a quantity of TPB in excess of that theoretically required to precipitate the cesium as cesium TPB. That excess is required partly because the significant amount of potassium present is also precipitated as potassium TPB, and partly because an excess of TPB in solution ensures more effective scrubbing of the radioactive cesium through precipitation. However, the benefit of effective scrubbing is accompanied by the generation of the benzene, which presents hazards of a different sort, and which also requires safety controls.

Westinghouse Savannah River Company is the Department of Energy contractor in charge of ITP. The Westinghouse staff at the Savannah River Site believed until recently that the principal cause of decomposition of TPB and generation of benzene is exposure of the TPB to the high level of radiation in the waste. That belief was based on results of full-scale tests conducted in 1983 that may have been misinterpreted, and on a decade of subsequent bench-scale tests using non-radioactive simulants (almost exclusively) rather than actual waste. The first large-scale operations with actual waste since 1983 were conducted recently in Tank 48, and they showed that the generation and release of benzene did not follow predictions. The generation of benzene in the waste under treatment in Tank 48 was unexpectedly rapid. A surprisingly large amount of the benzene remained captured in the waste, and that benzene was released through action of mixing pumps in the tank.

The current view of the contractor staff is that benzene is produced principally through catalytic decomposition of TPB ions in solution. They believe the catalysts are potentially both soluble and insoluble species, one of which is soluble copper known to be present in the waste.

They also believe that the cesium TPB precipitate and the potassium TPB precipitate are relatively immune to catalytic decomposition. The contractor proposes to conduct two Process Verification Tests (PVT), PVT-1 and PVT-2, to further establish the validity of these views and to demonstrate the accuracy of the model it has developed to predict the rate at which the captured benzene is released from solution. PVT-1 would be performed on the homogenized nuclear waste now in Tank 48, which has already been treated with TPB that subsequently has partly decomposed with the result that some cesium has returned to solution. Additional TPB would be added to this material to reprecipitate the cesium. The amount of TPB to be added would be strictly limited to a small amount as needed to reduce the concentration of cesium remaining in solution to a low radiation level acceptable for processing as low level waste in the saltstone process, and a large part of that solution would be sent to saltstone. The subsequent proposed experiment, PVT-2, will involve adding to the slurry remaining in Tank 48 a large amount of additional untreated waste and a substantial quantity of TPB as needed to precipitate the cesium in this new waste.

The Board has been informed that the primary safety precaution for the proposed cesium removal activities is to maintain an inert atmosphere in the headspace of Tank 48. This is to be done through establishing a sufficient flow of nitrogen to the tank. Two nitrogen feed systems are available, a normal system and a supplemental emergency system. The nitrogen systems are present to keep the concentration of oxygen below the level that would support combustion of the benzene. Westinghouse staff members have pointed out that these redundant inerting systems provide a sufficient safety factor for control of oxygen concentration in the headspace. They have further stated that the rate of buildup of oxygen concentration from air ingress into the tank headspace, if both inerting systems are simultaneously inoperable, would be slow enough to allow reestablishment of nitrogen flow before the bulk vapor in Tank 48 reaches the minimum oxygen concentration that could support combustion of benzene.

Operations since December 1995 indicate that for the current batch of waste, mixing pump operation increases the benzene release rate from the waste and that turning off the pumps essentially stops the release. The Board has been informed of the consequent belief that the actual rate of benzene release into the tank's headspace and its subsequent removal can be controlled through managing the action of the mixing pumps. This stratagem is to be followed in the tests as a means of maintaining the concentration of benzene in the headspace at a low enough level to prevent it from becoming flammable even if the oxygen concentration were to increase to an undesired level.

Westinghouse representatives also plan to impose a temperature limit for PVT-1 which is expected to prevent decomposition of TPB or to reduce its rate. Finally, they state that for PVT-1 the addition of TPB will be limited to 200 gallons of fresh 0.5 Molar sodium TPB solution, and that any subsequent additions during this experiment would be subject to review and approval by the Department of Energy. Westinghouse believes that this, in turn, would limit the maximum amount of additional benzene that could be produced. In effect, the amount of TPB added will be treated as an Operating Limit.

The Department and its contractor have brought substantial expertise to bear on understanding the science of the ITP process and the phenomena attending it. However, the Board is concerned that some important questions remain unanswered. First, the physical basis for holdup of large amounts of benzene in the waste and its removal through mixing pump operation is not yet well understood. Therefore, confidence in the ability to control its release is not as high as desired.

The Board is also concerned with the results of a recent laboratory-scale experiment using Tank 48 solution and TPB additive. The results from this experiment indicate that the amount of TPB which decomposed exceeded that amount which had been added during the experiment, suggesting that the cesium and potassium TPB precipitates had also partially decomposed, presumably through catalytic attack. If the cesium and potassium TPB precipitates were subject to rapid and extensive attack by a catalyst, an enormous amount of benzene could be generated, and the rate of release could be rapid enough to overwhelm the removal capability of the purging system for Tank 48.

The Board concurs with the view that ITP is of high value for subsequent vitrification of the nuclear waste in the tanks at the Savannah River Site, and that further testing is necessary to gain a better understanding of the science of the process to assure safety during and after precipitation of the cesium. The Board believes that if it were conducted according to the limitations stated above, PVT-1 can be run safely and can help in leading to an improved understanding of the science and the mechanisms involved in the ITP process.

The present plan for conduct of PVT-2 involves new and untested nuclear waste and a much larger addition of TPB. Furthermore, the liquid in Tank 49, which contains TPB from the previously mentioned 1983 demonstration test, is to be used as the source of a significant part of the TPB to be added to Tank 48 during PVT-2. The Board understands that Tank 49 was also the source of TPB used in the one experiment which led to an apparent decomposition of precipitated cesium and potassium TPB. One very probable interpretation of that anomaly is that the material in Tank 49 contains an unknown catalyst which can attack the precipitated material and might also increase the rate of release of benzene by an amount that is unpredictable at present. Furthermore, waste from tanks not yet tested could contain unknown constituents that could also adversely affect the rate of production and release of benzene.

The Board believes that the uncertainty in understanding of the science of ITP would make it imprudent to proceed from PVT-l to PVT-2 without substantial improvement in the level of understanding. Some such improvement may follow interpretation of the results of PVT-l. Better understanding of the anomalous experiment suggesting decomposition of TPB precipitates is also required.

Therefore, the Board makes the following recommendations:

1. Conduct of the planned test PVT-2 should not proceed without improved understanding of the mechanisms of formation of the benzene that it will generate, and the amount and rate of release that may be encountered for that benzene.

2. The additional investigative effort should include further work to (a) uncover the reason for the apparent decomposition of precipitated TPB in the anomalous experiment, (b) identify the important catalysts that will be encountered in the course of ITP, and develop quantitative understanding of the action of these catalysts, (c) establish, convincingly, the chemical and physical mechanisms that determine how and to what extent benzene is retained in the waste slurry, why it is released during mixing pump operation, and any additional mechanisms that might lead to rapid release of benzene, and (d) affirm the adequacy of existing safety measures or devise such additions as may be needed.

John T. Conway
Chairman

Appendix E - List of Potential Catalysts

Soluble Metals
copper (II)
molybdenum (VI)
chromium (VI)
silicon (IV)
selenium (VI)
arsenic (IV)
zinc (II)
lead (II)
iron (III)
tin (II)
mercury (II)
silver (I)
ruthenium (III)
palladium (II)
rhodium (III)
nickel (II)

Insoluble Metals
aluminum
iron
manganese
ruthenium
palladium
rhodium
chromium
copper
magnesium
nickel
lead
zinc
zirconium
uranium
plutonium
silver
cesium (tetraphenylborate)

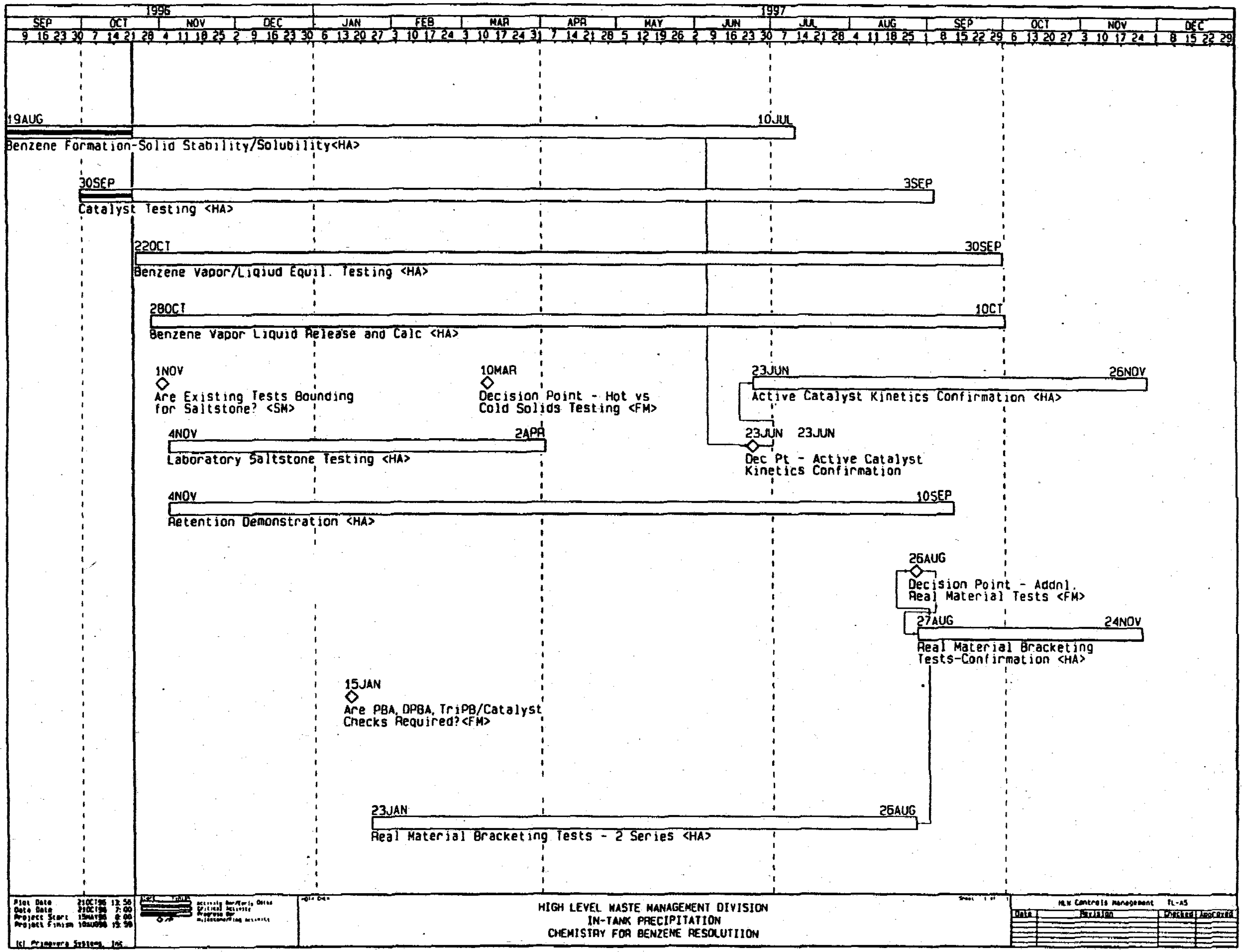
Organics
alcohols
benzene
triphenylboron hydroxy adduct
diphenylborinic acid
phenylboronic acid
other intermediates

Miscellaneous
monosodium titanate (MST)
MST w/insoluble metal species

Appendix F - Resource Loaded Schedule

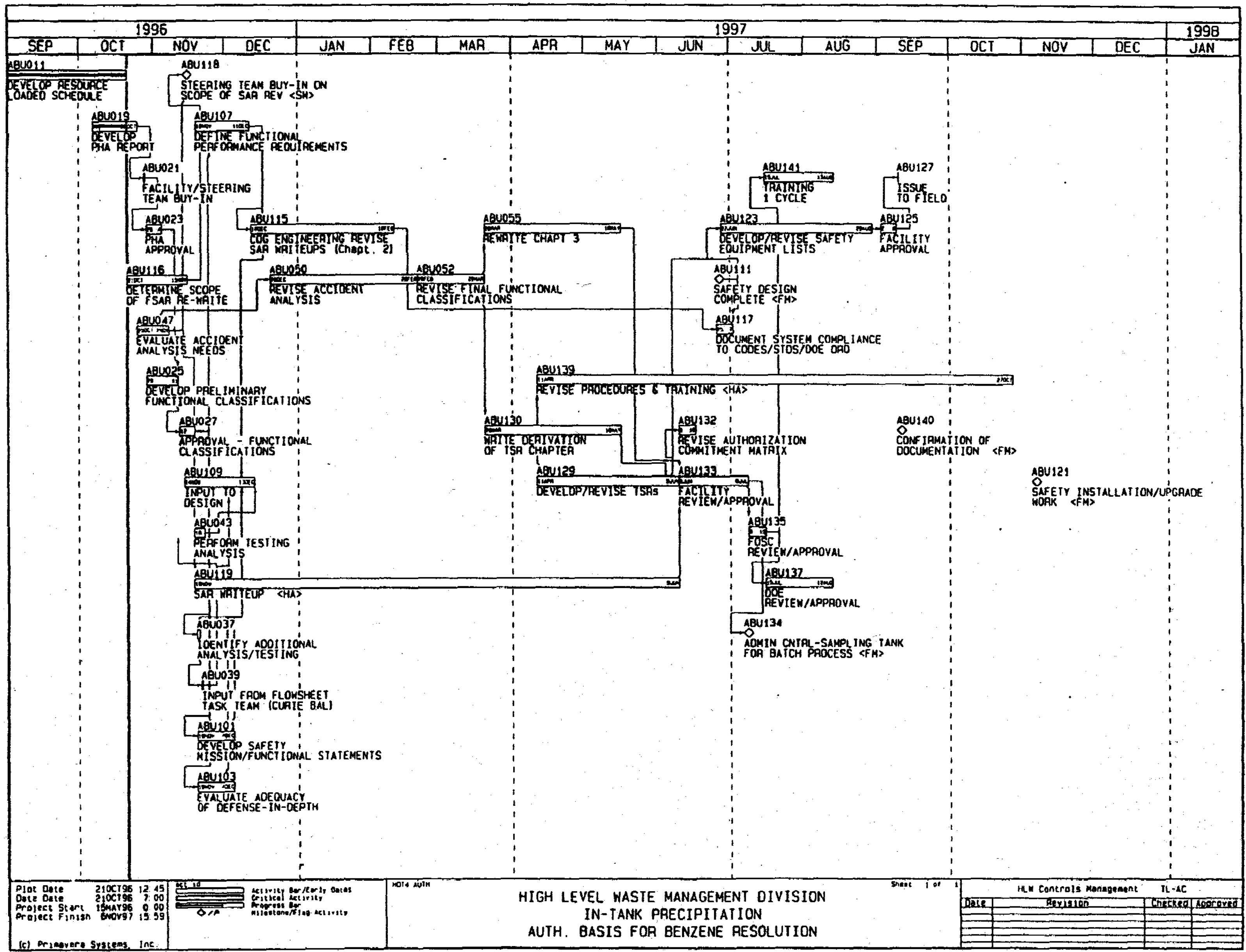
The schedule shown on pages F-2 and F-3 is part of an integrated Level 1 summary schedule of a much more detailed lower level schedule. Those activities with an <HA> suffix are hammocks, i.e., they are summary activities that electronically roll up more detailed lower level activities. As such, logic ties between some lower level activities are not shown. Resources have been applied to the schedule; both manpower and dollars. Many of the chemistry activities are loaded by individual researcher as these resources are very tight. Milestones for key decisions are also shown. These decisions affect either the direction of the chemistry program or whether a series of activities will be performed at all.

Appendix F - Resource Loaded Schedule

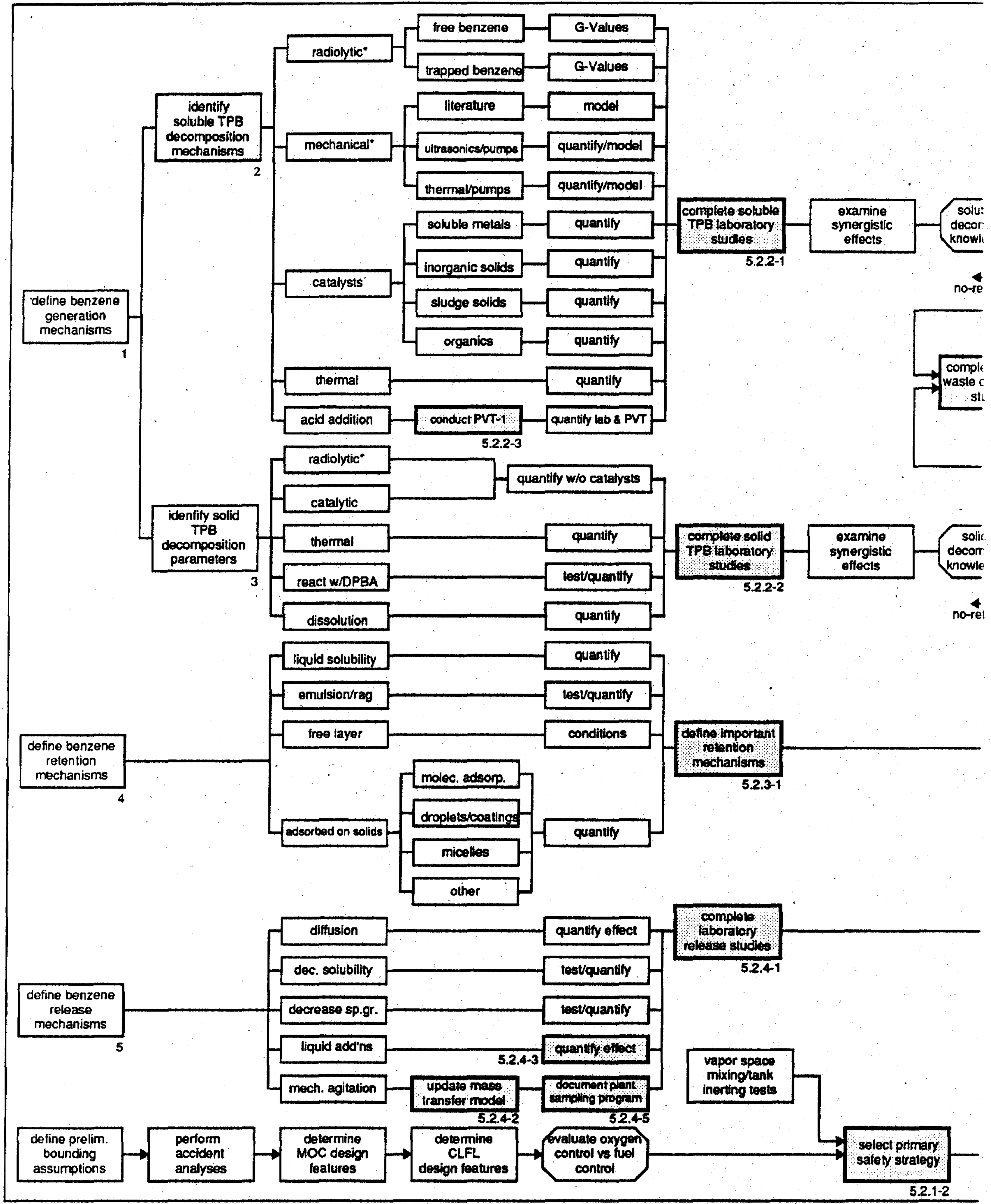


HIGH LEVEL WASTE MANAGEMENT DIVISION
IN-TANK PRECIPITATION
CHEMISTRY FOR BENZENE RESOLUTIION

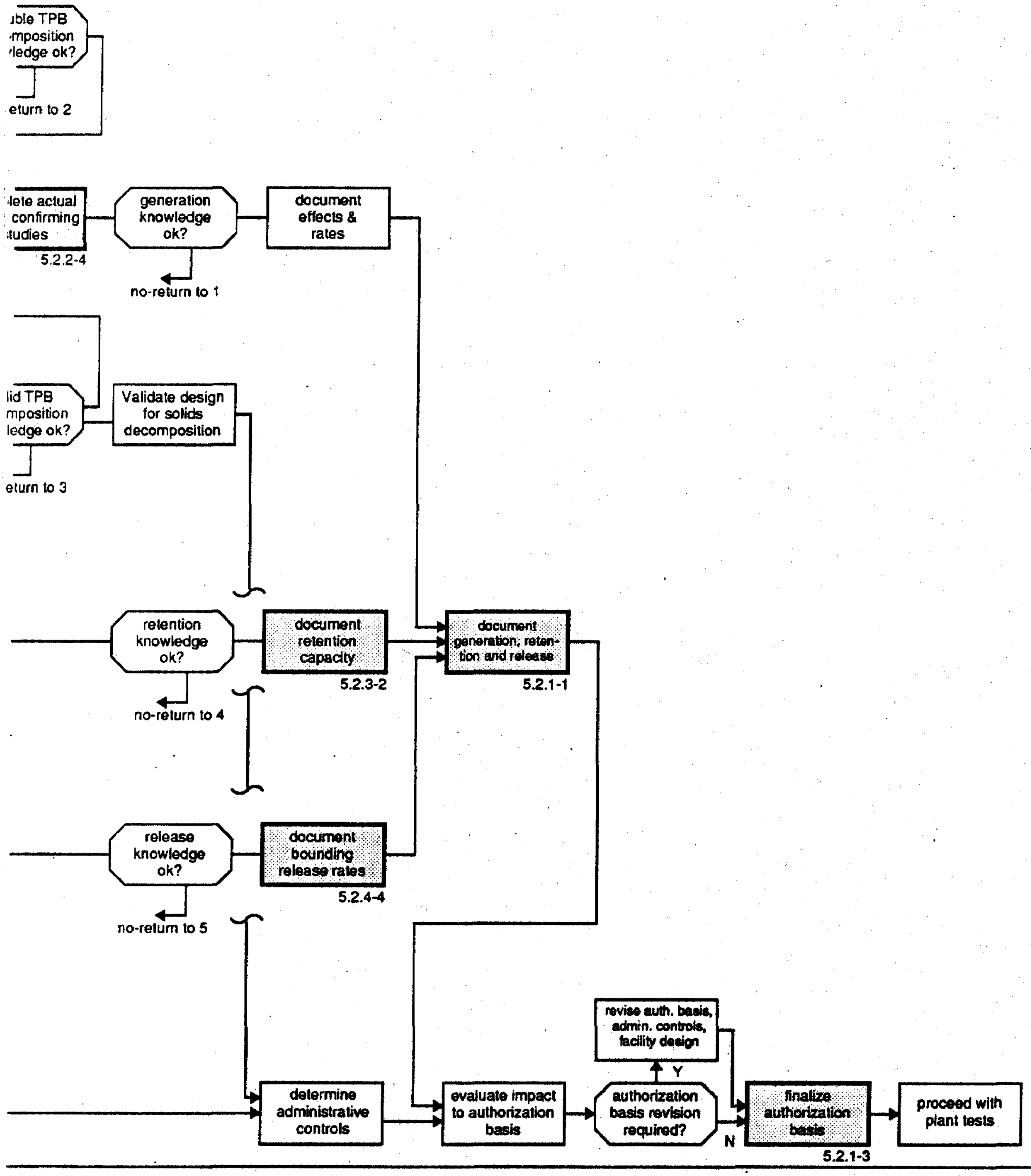
Appendix F - Resource Loaded Schedule



Appendix G - Simplified Program Logic Diagram



* note: adequate data exists for these mechanisms, however, they will be considered in the determination of the overall benzene generation rate


ıble TPB
ımposition
ıledge ok?
eturn to 2
ılete actual
confirming
ıtudies
5.2.2-4
generation knowledge ok?
no-return to 1
document effects & rates
lid TPB
mposition
ledge ok?
eturn to 3
Validate design for solids decomposition
retention knowledge ok?
no-return to 4
document retention capacity
5.2.3-2
document generation, retention and release
5.2.1-1
release knowledge ok?
no-return to 5
document bounding release rates
5.2.4-4
revise auth. basis, admin. controls, facility design
Y
determine administrative controls
evaluate impact to authorization basis
authorization basis revision required?
N
finalize authorization basis
5.2.1-3
proceed with plant tests

Appendix H - References

1. Benzene and Hydrogen Generation by Radiolysis of Tetraphenylborate Slurries - Interim Report #1, WSRC-TR-95-084, D. D. Walker to S. D. Fink, March 1, 1995.

2. Benzene and Hydrogen Generation by Radiolysis of Tetraphenylborate Slurries - Interim Report #2, WSRC-TR-95-190, D. D. Walker to S. D. Fink, May 22, 1995.

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

4. Hydrogen Generation by Radiolysis of Tetraphenylborate Solutions and Slurries, WSRC-TR-96-0109, D. D. Walker and C. L. Crawford to Distribution, June 19, 1996.

5. Stability of Spray-Dried Tetraphenylborate, WSRC-RP-94-774, M. J. Barnes to S. D. Fink, August 5, 1994.

6. Pump Degradation of Tank 48H Tetraphenylborate Slurry, WSRC-TR-96-0067, R. A. Peterson and R. F. Swingle to S. D. Fink, March 25, 1996.

7. Analysis of Benzene Formation During PVT-1 Oxalic Acid Filter Cleaning, HLW-ENG-96-0021, J. P. Morin to T. J. Lex, September 9, 1996.

8. Decomposition of Sodium Tetraphenylborate, WSRC-RP-90-465, M. J. Barnes to D. L. Fish, May 10, 1990.

9. Sodium Tetraphenylborate Solution Stability - A Long Term Study, WSRC-RP-92-786, M. J. Barnes to D. L. Fish, June 11, 1992.

10. Decomposition of Tetraphenylborate in Tank 48H, WSRC-TR-96-0113, D. D. Walker, et. al., to W. L. Tamosaitis, May 10, 1996.

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

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

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

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

Appendix H - References

15. Results from Tank 48H Slurry Decontamination and Decomposition Experiments in Support of ITP Process Verification Testing, WSRC-TR-96-0190, D. D. Walker, et al., to S. D. Fink, September 6, 1996.

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