97-0001501

Department of Energy
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DNF SAFETY BOARD

APR 28 1997

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

Dear Mr. Chairman:

SUBJECT: Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 96-1 Deliverable - Test Plan for Actual Waste Confirming Studies

Enclosed is the subject test plan which provides a scheduled deliverable (Commitment 3, Milestone 5.2.2-4) in accordance with the DNFSB Recommendation 96-1 Implementation Plan. This test plan is issued as Appendix E of the "Test Program for Resolution of DNFSB Recommendation 96-1" document (HLW-OVP-97-0009), which was transmitted to you on January 28, 1997.

This test plan describes testing activities to be performed in the Shielded Cells at the Savannah River Technology Center using real radioactive waste materials from the High Level Waste Tank Farms. These tests will explore benzene generation at realistically bounding process conditions for the remaining steps of In-Tank Precipitation (ITP) Cycle 1. The results will be used to confirm that the benzene generation rates developed from simulant studies and used in the ITP Authorization Basis bound the behavior of the real waste material.

The U.S. Department of Energy, Savannah River Operations Office, has completed the actions for the first deliverable identified under Milestone 5.2.2-4. The commitments under this milestone will not be completely met until the Actual Waste Confirming Studies have been completed and the second deliverable (Report on Actual Waste Confirming Studies) has been issued in September 1997. Copies of the subject deliverable have been provided and discussed with your staff.

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

Sincerely,

Ray J. Achgren for

Frank R. McCoy
Assistant Manager
for High Level Waste

ED:JWM:eeh

PC-97-0043

Enclosure:
Appendix E: Test Plan for Actual Waste
Confirming Studies

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APPENDIX E:

TEST PLAN FOR ACTUAL WASTE CONFIRMING STUDIES

DNFSB 96-1 IMPLEMENTATION PLAN COMMITMENT #3, MILESTONE #5.2.2-4

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ADC & Reviewing Official: J. Barnick
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1.0 Introduction & Background

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

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

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

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

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

Implementation Plan Commitment # 3 includes the experimental program related to the scientific understanding of benzene generation. Milestones 5.2.2-1 and 5.2.2-2 cover decomposition of soluble and solid TPB, respectively, and are discussed in Appendices A and B. Milestone 5.2.2-3 is complete by issuing the PVT-1 test report in March, 1997. The final Milestone in Commitment #3 is 5.2.2-4 which covers studies to confirm benzene generation from actual waste. The Implementation Plan states "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." This test plan describes the planned actual waste studies.

2.0 Scope

The scope of this test plan covers activities performed by the Waste Processing Technology Section (WPTS) of the Savannah River Technology Center (SRTC) and the Shielded Cells Operations of the Technical Services Division (TSD/SCO). These activities involve tests in the Shielded Cells using radioactive materials from the tank farm. These tests will explore benzene generation at realistically bounding process conditions for the remaining steps of ITP Cycle 1. The results will be used to confirm that correlations developed from simulant tests are consistent with benzene generation rates observed in real waste tests and that benzene generation rates used in the ITP Authorization Basis are sufficiently bounding to complete ITP Cycle 1.

This test plan describes studies of benzene generation from actual ITP Cycle 1 wastes at realistically bounding process conditions. ITP Cycle 1 Tests will step through the sequence of events that will occur in the plant, using the actual waste materials for the remainder of the first cycle, with parameters that bound expected operating conditions; that is, parameters will be set at the high end of the ranges used to develop the proposed Authorization Basis.[a] [7.3] The Cycle 1 tests will verify that correlations developed during simulant testing hold with real waste at the limit of the conditions expected for Cycle 1 operation. The ITP Cycle 1 tests will include all actual operations (precipitation, filtration, washing), in batch-sequence processing, using realistic cycle times for these events. The remainder of the ITP Cycle 1 sequence starts with Batch 2 precipitation and concentration (Batch 1 is already complete), continuing through precipitation and concentration of Batches 3 and 4, and concluding with precipitate washing.

Benzene generation from three portions of the ITP process will be monitored during these tests: Tank 48H slurry, decontaminated salt solution, and ITP wash water. The benzene generation rate will be monitored directly by measuring the benzene evolved and/or indirectly by tracking the decomposition of soluble TPB and its decomposition intermediates.

3.0 Objectives and Expectations

3.1 Objectives: The tests outlined in this test plan will determine benzene generation rates for ITP Cycle 1 at realistically bounding process conditions. A Technical Task Request (TTR)[7.4] has been issued by ITP Engineering (ITP-E) defining the specific tasks for this plan. The tasks stated in the TTR are:

3.1.1 Perform Cycle 1 demonstration testing, including determination of sodium titanate loading, required excess TPB, inclusion of 1983 demonstration

[a] Several parameters potentially affect the rate of TPB decomposition and the resulting benzene generation rate: catalytic species and sludge in the salt solution feeds (*i.e.*, batch composition), temperature, and soluble TPB concentration. After the batch is constituted, the bounding, controllable process parameters are temperature and soluble TPB. Sludge solids will be added in excess of the current Process Requirements limit; temperature and soluble TPB concentration will be at the limit of the proposed Authorization Basis.

wash water stored in Tk 49, and determination of Cs decontamination and benzene generation rates. Batch composition will approximate the recipe to be used for the balance of ITP Cycle 1.

3.1.2 Determine benzene generation source term based on bounding reaction conditions.

3.1.3 Confirm correlations from previous simulant testing using actual waste.

3.1.4 Concentrate and wash precipitate, measure Cs-137 concentrations and monitor soluble TPB and intermediates decomposition.

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

3.2.1 The remaining steps of ITP Cycle 1 will have been performed sequentially using the actual radioactive materials scaled to approximate the batch recipe to be used for the balance of ITP Cycle 1.

3.2.2 The benzene generation rate will have been determined at realistically bounding process conditions for each remaining ITP Cycle 1 step.

3.2.3 The predicted Cs activities will have been confirmed.

3.2.4 The required sodium titanate quantity will have been determined.

3.2.5 The benzene generation rates for ITP Cycle 1 determined in these tests will be within the rates used in the proposed Authorization Basis.

3.2.6 Use of simulants for testing and development will have been validated by comparison to tests using real wastes.

4.0 Test Methodology and Approach

4.1 A Task Technical Plan (TTP) has been prepared by WPTS to control the work related to this test plan.[7.5] To produce the expected results, key parameters for these shielded cell tests must be selected and controlled. The key parameters are batch composition, excess NaTPB, sludge concentration, temperature, time, agitation, and purge/atmosphere. Other parameters which may influence results are organics and precipitation time.

4.1.1 Batch composition is a key variable for the ITP Cycle 1 tests. The feed batch and slurry will be prepared by a recipe scaled to the case designated as "Space Gain, Tank 25" in the most recent waste removal plan.[7.6] Any changes to the scaled recipe require written concurrence from High Level Waste Engineering (HLWE). Samples will be analyzed at appropriate points to ensure adequate characterization for slurry preparation and to confirm initial composition.

4.1.2 Based on current understanding, the overwhelming source of benzene generation is the soluble (excess) NaTPB added to obtain and maintain Cs concentrations low enough to permit production of decontaminated salt solution. The proposed Authorization Basis uses preliminary calculations of benzene generation rates documented in Reference 7.7. In these calculations, the initial soluble TPB after precipitation is 0.00238 M,[b] which is approximately 100% of saturation for a 4.7 to 5 M salt solution. The current ITP plans are to operate at about 50% of this quantity, or about 0.0012 M excess (soluble) NaTPB.

4.1.3 Preliminary catalyst ID studies implicate sludge as a key source of catalytic activity[7.8] Sludge collected with the waste samples used in these tests will be added in amounts which exceed the maximum expected concentration. The target for sludge concentration in these tests is about 1 g/L on an added salt solution basis which is about 2.5 times higher than the current ITP Process Requirement limit of 400 mg/L.[7.9] (The basis for the PR limit is prior experiments which showed reduced crossflow filter performance at increasing sludge concentrations.) If there is insufficient sludge in the feed samples to approach the target concentration, real waste sludge matching the sludge type in the tested salt solutions will be added.

4.1.4 Temperature is of course a critical parameter since reaction rates vary exponentially with temperature. As presented in the safety strategy,[7.3] ITP will be operated at a temperature which will limit decomposition of soluble TPB. The Authorization Basis is currently expected to limit ITP operating temperature below 45 °C. For these tests, the temperature will, therefore, be held at 45 °C. The ITP Cycle 1 test will use a constant temperature bath to control the temperature. The temperature control range for this particular bath has not yet been characterized but it is expected to control within ± 2 °C except during certain operations such as batch preparation, water addition to replace evaporation, or concentration steps.

4.1.5 The most important time increments with respect to benzene generation are those associated with concentration and production of decontaminated salt solution. These are the longest periods at the highest soluble TPB concentrations. During the ITP Cycle 1 test, the hold period following the first precipitation (Batch 2 of Cycle 1) will be four weeks, which is slightly longer than anticipated during plant operation. Planned hold times for Batches 3 and 4 will be three and two weeks, respectively, but times may

[b] For the calculations, Taylor added NaTPB at 117% of 0.014 M K^+. This results in an excess of 0.00238 M NaTPB (Cs is ignored).

be adjusted as necessary based on the benzene generation and/or soluble TPB decomposition measured in the first test.

4.1.6 Soluble or slightly soluble organics such as decomposition intermediates and benzene have recently been identified as playing a role in TPB decomposition. Currently, Tank 48H has low concentrations of these organics; therefore, the initial organics concentration in these tests will be low (which is consistent with ITP Cycle 1). However as TPB decomposes due to test conditions such as high soluble TPB concentration, temperature, and time, the organics concentrations will accumulate to a peak following the final precipitation step.

4.1.7 Even though Tank 48H will not be agitated continuously, continuous agitation of the slurry during the ITP Cycle 1 test is expected to produce maximum benzene generation (reaction) by promoting good mixing and reactant contact. More importantly, continuous agitation will promote smooth and continuous evolution of benzene as it is generated, thus preventing significant benzene retention and periodic release. This is particularly important because the benzene generation rate will be measured by periodic sampling of the off gas from the continuous purge.

As discussed in 4.1.6, releasing the benzene as it is formed may reduce the rate of TPB decomposition. A portion of the Batch 2 preparation will be placed in a static container sealed under N_2 and placed in the constant temperature bath with the purged slurry. In parallel, the concentration of soluble TPB and its intermediates will be monitored in the static sample and compared to the purged and agitated slurry. If the static sample indicates that the continuous release of benzene reduces the rate of soluble TPB decomposition, the experimental procedure will be revised for Batches 3 and 4. If this change is required, monitoring TPB decomposition rate by measuring benzene generation rate will no longer be feasible.

4.1.8 Recent tests have implicated the role of oxygen in catalyst activation and soluble TPB decomposition in the ITP process.[7.1,7.10] The presence of O_2 is associated with an induction period while TPB decomposition tends to initiate rapidly in the absence of O_2. The slurry in Tank 48H is expected to be essentially anoxic due to: N_2 purging ($\leq$ 5% O_2 in the head space), occasional agitation with relatively poor mass transfer of O_2 from the vapor to the slurry, and liquid phase reactions which scavenge the small quantity of soluble O_2. Therefore, these tests will be maintained anoxic by purging with N_2.

4.1.9 When substantial soluble TPB is present, benzene generation from radiolysis is typically quite small compared to TPB decomposition. However, radiation may have a chemical effect on the benzene generation rate; for example, by the formation of free radicals. Studies of benzene generation with simulants have not yet included radiation as a parameter. Since the ITP Cycle 1 tests will include radioactive wastes, radiation will be an embedded parameter (although, any effect of radiation is likely to be reduced by the small experimental geometry). If radiation has an effect, it will be difficult to discern it from other parameters except that rates might be higher (or lower) than expected; however, scheduled simulant studies will include tests to determine if radiation affects the rate of soluble TPB decomposition. (See Section 6.3 for further discussion.)

4.1.10 Recent experience has also shown that rate and conditions of NaTPB addition are known to have strong influence on K and Cs precipitation (*i.e.*, sufficient decontamination) and formation of NaTPB precipitate in unsaturated solutions. To avoid this problem, NaTPB will be added slowly with good agitation to minimize local or global saturation of the solution. Depending on the quantity to be added, NaTPB will be delivered dropwise over a period of four to eight hours.

4.1.11 For the purposes of the ITP Cycle 1 demonstration, sodium titanate will be added during these tests based on the characterization performed on the feed samples. Sodium titanate requirement tests, which confirm sufficient salt solution decontamination for Saltstone Production Facility feed, is part of the TTR[7.4] and TTP,[7.5] but is not required for resolution of DNFSB 96-1. Sodium titanate addition to Tank 48H may have to be adjusted based on the requirement tests, but this would not affect the ITP Cycle 1 test outcome since recent catalyst identification studies have removed titanate from the list of potential catalysts.

4.2 The ITP Cycle 1 test will be performed sequentially to duplicate the batch steps planned for the balance of Cycle 1 (Batches 2, 3, and 4; Batch 1 is already complete).[7.6] The benzene generation will be characterized during the periods of highest soluble TPB concentration which occur following NaTPB addition and during the concentration steps. The "benzene generation rate" will be monitored both directly by periodic measurement of the benzene concentration in the continuous off-gas flow and indirectly by tracking the decomposition of soluble TPB and its intermediates. The slurry will then be washed to confirm predicted Cs-137 activity at low Na^+ concentrations. Additionally, filtrate from both the final precipitation and concentration and from washing will be characterized for benzene generation by tracking decomposition of soluble TPB and its intermediates. In another portion of the experiment, the stability of TPB solids will be monitored. The experimental planned approach for these tests is:

4.2.1 For ITP Cycle 1, Batch 2 (Batch 1 is already complete, Batches 2, 3, and 4 complete Cycle 1): Combine the feeds scaled to the specified recipe for Batch 2; add NaTPB to achieve about 0.0024 M excess NaTPB; agitate continuously and hold at 45 °C; purge with N_2; hold for four weeks; monitor the benzene generation rate and concentrations of soluble TPB and decomposition intermediates at the intervals specified in the TTP; concentrate to the desired volume for the next step.

4.2.2 For ITP Cycle 1, Batch 3: Repeat the previous step using the Batch 3 recipe except that the hold period is three weeks.

4.2.3 For ITP Cycle 1, Batch 4: Combine the feeds scaled to the specified recipe. Add stoichiometric NaTPB to a portion of the slurry (solids stability study described in 4.2.4 below). To the remainder of the slurry, add NaTPB to achieve about 0.0024 M excess NaTPB (benzene generation study described in 4.2.5 below).

4.2.4 For the solids stability study, hold at 45 °C sealed under N_2 and agitate by shaking periodically; monitor solids stability by sampling the slurry for Cs-137 activity and concentrations of soluble TPB and decomposition intermediates at the intervals specified in the TTP.

4.2.5 For the benzene generation study, agitate continuously and hold at 40 °C; purge with N_2; hold for two weeks; monitor the benzene generation rate and concentrations of soluble TPB and decomposition intermediates at the intervals specified in the TTP; concentrate to the desired volume for the next step.

4.2.6 Hold filtrate from the previous step at 45 °C under air and monitor for concentrations of soluble TPB and decomposition intermediates.

4.2.7 If necessary, adjust the soluble TPB in the material from step 4.2.5 to that anticipated at the start of washing and then wash the slurry; hold selected wash water samples at 45 °C under air and monitor for Cs-137 activity and concentrations of soluble TPB and decomposition intermediates.

5.0 Test Description

The ITP Cycle 1 test will be conducted using radioactive wastes from the F and H Tank Farms. The experiments will be performed in the Shielded Cells facilities in SRTC, which are capable of handling the highly radioactive materials required for these tests. The experiments are performed remotely in equipment which is operated by manipulators. The complexity of the experimental equipment, procedures, and sampling are thus constrained by the operating and experimental environment. Experiments must be designed to be as simple as possible while still achieving the experimental objectives.

The ITP Cycle 1 test will be performed using samples taken from the tanks which will be used to complete Cycle 1 in the plant. As recommended in Ref. 7.6, the required samples are Tank 48H (ITP Batch 1/Cycle 1), Tank 49H (wash water from the 1983 ITP demonstration), and fresh wastes from Tanks 25F, 32H, 34H,[c] and 39H which will be provided by the HLW Division to the Shielded Cells. If additional sludge solids are needed, these can be obtained from sludge samples already in inventory in the Shielded Cells. Any changes to the scaled recipe require written concurrence from HLWE.

5.1 Cycle 1/Batch 2

5.1.1 On a scaled basis per Ref. 7.6, combine materials to produce a pre-strike slurry;[d] sample and analyze to characterize; add sludge if necessary to meet target concentration.

5.1.2 Add NaTPB to achieve about 0.0024 M excess NaTPB.

5.1.3 Place in a constant temperature bath with N_2 purge and agitate with a magnetic stir bar. Place a portion of the slurry in a static, sealed container in the same constant temperature bath.

5.1.4 Hold at 45 °C under N_2 purge with continuous agitation for four weeks; sample and analyze the vent gas for benzene at the intervals specified in the TTP; sample and analyze the purged, agitated slurry for soluble TPB, decomposition products, and total soluble boron at least once per week. Sample and analyze the static slurry for soluble TPB and decomposition products after three weeks of hold time. (Total soluble boron may be discontinued for all but the final sample if all NaTPB is dissolved.)

5.1.5 Concentrate slurry to produce the required scaled volume.

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[c] Material from Tank 34H will be transferred to Tank 39H before the 39H transfer to ITP.

[d] Pre-strike is prior to the addition of NaTPB in a given step.

5.2 Cycle 1/Batch 3

NOTE: If indicated by the results of the static Batch 2 slurry sample, the procedure for 5.2 and 5.3 will be modified to retain benzene in the slurry.

5.2.1 On a scaled basis per Ref. 7.6, combine the slurry from step 5.1.5 with fresh waste to produce a pre-strike slurry; sample and analyze to characterize; add sludge if necessary to meet target concentration.

5.2.2 Add NaTPB to achieve about 0.0024 M excess NaTPB.

5.2.3 Place in a constant temperature bath with N_2 purge and agitate with a magnetic stir bar.

5.2.4 Hold at 45 °C under N_2 purge with continuous agitation for three weeks;[e] sample and analyze the vent gas for benzene at the intervals specified in the TTP; sample and analyze the slurry for soluble TPB, decomposition products, and total soluble boron at least once per week. (Total soluble boron may be discontinued for all but the final sample if all NaTPB is dissolved.)

5.2.5 Concentrate slurry to produce the required scaled volume.

5.3 Cycle 1/Batch 4

5.3.1 On a scaled basis per Ref. 7.6, combine the slurry from step 5.2.5 with fresh waste to produce a pre-strike slurry; sample and analyze to characterize; add sludge if necessary to meet target concentration.

5.3.2 To an aliquot of the slurry, add stoichiometric NaTPB (this sample will be monitored for solids stability); sample and analyze to confirm additions and starting concentrations.

5.3.3 To the remaining slurry, add NaTPB to achieve about 0.0024M excess NaTPB (this sample will be monitored for benzene generation rate).

5.3.4 Place the solids stability sample sealed under N_2 in an oven at 45 °C for four weeks; monitor solids stability by sampling the slurry for Cs-137 activity and concentrations of soluble TPB and decomposition intermediates at least weekly.

5.3.5 Place the benzene generation sample in a constant temperature bath; hold at 45 °C under N_2 purge with continuous agitation for two weeks; sample and analyze the vent gas for benzene at the intervals specified in the TTP;

[e] Based on results of Cycle 1/Batch 2, the hold period may be adjusted to as little as two weeks or extended if necessary. The frequency of slurry samples will be adjusted to ensure that at least three slurry samples are obtained after the start of the hold period.

sample and analyze the slurry for soluble TPB, decomposition products, and total soluble boron at least once per week. (Total soluble boron may be discontinued for all but the final sample if all NaTPB is dissolved.)

5.3.6 Concentrate slurry from step 5.3.5 to produce required scaled volume.

5.3.7 Hold a portion of the filtrate from step 5.3.6 at 45 °C under air and monitor for decomposition of soluble TPB and its intermediates.

5.4 Cycle 1/Washing

Washing will be performed to confirm predicted Cs-137 concentrations at reduced [Na^+] by batch dilution and concentration rather than continuous washing as in the plant. The slurry will be diluted by a factor of three and then concentrated to the original volume. This will be repeated five times. The final [Na^+] should be < 0.05 M. Washing will be performed at ambient Shielded Cell temperature to reduce the rate of soluble TPB decomposition.

5.4.1 Using the slurry from step 5.3.6, if necessary adjust the soluble TPB to the concentration expected at the start of washing; sample and analyze to confirm additions and starting concentrations.

5.4.2 Add inhibited water to dilute by a factor of three and hold long enough to ensure Cs/NaTPB equilibrium.

5.4.3 Filter to the volume at the start of step 5.4.2.

5.4.4 Analyze the filtrate for Cs-137 activity and for concentrations of soluble TPB and decomposition intermediates.

5.4.5 Repeat steps 5.4.2 to 5.4.4 until washing is complete.

5.4.6 Hold selected filtrates from step 5.4.3 at 45 °C under air and monitor for decomposition of soluble TPB and its intermediates.

6.0 Evaluation of Results, Expected Ranges, and Unexpected Results

6.1 Evaluation of results

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

6.2 Expected range of results

- Benzene generation rate
  Preliminary calculations performed by Taylor lead to an estimated maximum benzene generation rate of 0.92 mg/L-hr.[7.7,7.11] This information was provided as the basis for initial development of the Authorization Basis. As more refined information becomes available through the chemistry program, the initial estimate is being revised. The current results suggest a bounding benzene generation rate in Tanks 48 and 49 of 0.35 mg/L-hr, and a nominal flowsheet benzene generation rate in those tanks of 0.21 mg/L-hr.[7.12] These calculations will be further modified, and the final result incorporated into the Authorization Basis. The benzene generation rates measured and inferred in the ITP Cycle 1 tests are expected to be consistent with the nominal flowsheet benzene generations rates, and are not expected to exceed the calculated bounding rates.

- Solid TPB stability
  The ITP Cycle 1 tests will produce data on the stability of solid TPB. This data will be compared to results from tests being peformed by D. D. Walker.

- Cs solubility
  Cs-137 activity will be monitored to confirm anticipated concentrations in decontaminated salt solution and in wash water. At the projected soluble TPB concentrations, the Cs-137 activity in the decontaminated salt solution is expected to be less than 35 nCi/g (the limit for transfer to the Saltstone Production Facility) and less than about 9,600 nCi/g for wash water at the end of washing (approximately the design bases for shielding in the ITP and Late Wash analytical labs).

6.3 Unexpected results

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

- ITP Cycle 1 test benzene generation greater than Authorization Basis.
  A measured benzene generation rate which exceeds the Authorization Basis could be due to several possibilities: the simulants did not include all active catalytic species, radiation causes additive or synergistic reactions (*e.g.*, increased free radicals), sludge solids present in greater than previously tested amounts, or poor experimental temperature control. This result would likely have significant programmatic effect including delaying resumption of operations. Additional work could include both experimental and physical modifications. Experiments may be required to explore the effectiveness of potential process changes (*e.g.*, lower temperatures or sludge solids removal) or reaction of simulants in a radioactive field to identify the cause of the

higher rates. Physical modifications could include changes such as filtration to remove sludge solids, process cooling to further reduce operating temperatures, or N_2 inerting on Tank 50H.

- ITP Cycle 1 test benzene generation less than Authorization Basis.
  Benzene generation and soluble TPB decomposition rates will be compared to updated rates based on the results of the latest simulant tests. If the rates are significantly lower than expected, the test procedures and results will be carefully reviewed; possibly including additional analyses of retained test samples. If the review does not pinpoint the reason for reduced rates, repeat testing will likely be required. If after thorough review the benzene generation rates are confirmed to be significantly less than the Authorization Basis, there may be opportunities to reduce the scope of the physical modifications and/or run the process at somewhat less constraining conditions.

- Cs concentrations higher than expected.
  The impact of higher than expected Cs concentrations depend on how much and where. For example, activity of 50 to 85 nCi/g in the decontaminated salt solution could be handled with additional shielding at key locations in the Saltstone facilities. If benzene generations rates are relatively low, the process could be operated at higher soluble TPB concentrations to suppress Cs solubility.

- Failure to reach precipitation equilibrium in a short period of time.
  Experience indicates the technique for adding NaTPB affects potassium and cesium precipitation. The experimental technique will be designed to reduce the possibility of this occurrence. However, if it does occur it would be easily identified in the Cs-137 activity of the early filtrate samples. If so, the experiment may have to be restarted which would involve obtaining additional waste samples from the Tank Farm.

- Long induction period.
  As previously discussed in section 4.1.7, the presence of air in solution has been associated with an induction period. The experiments will be performed under N_2 inerting to eliminate or minimize any induction period. However, if an induction period does occur, it would be detected by much lower than expected benzene generation rates for some period of time. The impact would be extension of the hold periods, possibly extending the tests by several weeks. Also, an extended hold period would call for more samples which could deplete the experimental stock, requiring additional waste samples from the Tank Farm. In either case, this would have significant programmatic impact since these tests are on the schedule critical path.

7.0 References

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

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

7.3 M. J. Montini, *ITP Safety Strategy for Tanks 48, 49, and 50 Deflagrations (U)*, WSRC-TR-97-0003, Rev. 0, January 1997.

7.4 HLE-TTR-97014, Rev. 1, *Actual Waste Studies for DNFSB 96-1 (U)*, March 26, 1997 .

7.5 D. D. Walker and D. T. Hobbs, *Task Technical Plan for Radioactive Tests in Support of the In-Tank Precipitation Facility (U)*, WSRC-RP-97-0059, April 1997.

7.6 G. A. Taylor, *Feed Stocks for the Remainder of ITP Cycle 1 (U)*, HLW-HLE-97-0046, February 1997.

7.7 G. A. Taylor, *Preliminary ITP Flowsheet Calculations (U)*, HLW-HLE-96-0410, December 1996.

7.8 M. J. Barnes, C. L. Crawford, and C. A. Nash, *Sodium Tetraphenylborate Catalyst Identification: Preliminary Studies Set (U)*, WSRC-TR-97-0060, Rev. 0, March 1997.

7.9 Process Requirement limit 3.1.1.1, L18, *Composition Limits Incoming to Tank 48H, WSRC-IM-91-63 (U)*, Rev. 8, September 1996.

7.10 M. L. Hyder, *The Role of Oxygen in the Copper-Catalyzed Decomposition of Phenyl Borates in Aqueous Alkaline Solutions (U)*, WSRC-TR-97-0069, Rev. 0, March 1997.

7.11 P. L. Rutland, *Preliminary Bounding Benzene Generation Rates (U)*, HLW-HLE-96-0425, December 1996.

7.12 P. L. Rutland, *Revised Preliminary Benzene Generation Rates (U)*, HLW-HLE-970141, April 1997.

8.0 Attachments

None.