[DOE (SROO) LETTERHEAD]

MAR 10 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 Summary Report for Process Verification Testing

Enclosed is the Test Summary Report for the Process Verification Test (PVT-1) which is a deliverable defined in the Implementation Plan for DNFSB Recommendation 96-1 (Commitment number 3, Milestone 5.2.2-3). This test report summarizes the objectives, procedures, results and conclusions of the PVT-1.

The U.S. Department of Energy, Savannah River Operations Office, has completed the actions necessary for milestone 5.2.2-3 and proposes its closure. Copies of the deliverable have been provided and discussed with your staff. Please direct any questions to me or W. F. Spader at (803) 208-7409.

Sincerely,

A. Lee Watkins
Assistant Manager for High Level Waste

ED:JWM:kl

PC-97-0027

Enclosure:
Process Verification Test, Test Summary Report

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PROCESS VERIFICATION TEST

TEST SUMMARY REPORT

March 3, 1997

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1.0 PURPOSE AND GENERAL DESCRIPTION OF THE TEST

This "Process Verification Test, Phase 1" (PVT-1) was performed to provide information for the resolution of benzene generation and evolution issues associated with the In-Tank Precipitation (ITP) process. Testing in Tank 48 focused on the effect of adding a known quantify of sodium tetraphenylborate (NaTPB) to reduce the concentration of soluble Cs-137; concentrating the resulting slurry using normal process equipment and systems; and chemically cleaning the process filter including draining of oxalic acid (OA) to Tank 48.

Specific objectives of the test follow:

- Demonstrate the capability of precipitating the Cs-137 in Tank 48 to a level that meets the Process Requirements criteria for transfer to Tank 50.
- Monitor the decomposition of soluble NaTPB added to Tank 48 and correlate product decomposition with analytical and experimental models. (Ref. 9.1)
- Compare the bounding benzene mass transfer model predictions with measurements during periodic operation of the slurry pumps.(Ref. 9.2 and 9.3)
- Assess filter performance.
- Monitor the effect of adding oxalic acid to Tank 48 during filter cleaning.

2.0 PROGRAM OVERVIEW

The In-Tank Precipitation process decontaminates radioactive salt solutions by addition of sodium tetraphenylborate to precipitate soluble salts of cesium and potassium. The resulting slurry is filtered and the decontaminated filtrate processed as low level waste while the concentrated precipitate is processed into high level waste glass. A safety issue has been raised regarding the production of benzene as a by-product of TPB decomposition. The PVT-1 is part of the program to resolve this safety issue.

The PVT-1 focused on Tank 48 chemistry and was conducted in such a way as to minimize the spread of benzene safety issues to Tank 50 (Ref. 9.4). The NaTPB decomposition reaction is known to consume all of the excess NaTPB, but induction time, benzene yield, and release rate may depend on variables such as the availability of oxygen, liquid temperature, and copper ion and sludge solids concentration. For PVT-1, copper and sludge solids content remained constant and the vapor space oxygen concentration, liquid temperature, water additions, and excess NaTPB were controlled and monitored.

A relatively small amount (288 gallons, compared to a total slurry volume of 234,000 gallons) of NaTBP, with an average Molarity of 0.59, was added to Tank 48. The NaTPB added was approximately double the stoichiometric amount required to precipitate the very low concentration of Cs and K that was in solution at the time of the addition. (Note that the majority of the Cs and K in Tank 48 had been precipitated during prior operations and remained as CsTPB and KTPB.) The amount of NaTPB added was selected to provide a soluble excess TPB concentration large enough to elicit a system response. The testing consisted of monitoring for the following: (See Table 1 for sampling information)

- Decomposition of the added NaTPB - Decomposition was detected by changes in soluble NaTPB, and reaction product concentrations.

- Precipitation of Cs-137 - Precipitation of Cs-137 was expected to reduce Cs-137 to less than 85 nCi/gram. This low Cs-137 concentration was expected to be maintained for 18 to 20 days (432 to 480 hours), until TPB concentration dropped to below 50 mg/L.

- Benzene mass transfer - Increases in benzene vapor concentration from NaTPB decomposition and subsequent release during pump runs, and losses out the purge exhaust and stack were monitored.

- Filter performance - Full scale testing was required to verify that the decomposition of NaTPB had no significant impact on filter performance and cleaning. No measurable loss in filter performance was expected.

- Oxalic acid addition to Tank 48 - During the filter cleaning approximately 250 gallons of oxalic acid was added to Tank 48 along with water flushes and caustic additions. Benzene could be formed by acid hydrolysis of TPB salts if the tank were not well mixed. No significant benzene formation was expected.

3.0 SUMMARY

3.1 Test Procedures and Approach

Testing was conducted using Standard Operating Procedures (SOP's) and Integrated Operating Procedures (IOP's) for the normal operations of the plant equipment. One Special Procedure, SP-96-ITP-054, "Adding NaTPB From Drums To Tank 48 (U)", was used to add the NaTPB to Tank 48. Special instrumentation in the form of Gas Chromatographs (GC's) with a Data Acquisition System (DAS) was connected to two "instrument trees" inserted into the Tank 48 vapor space. The instrument trees enabled the analysis of localized vapor composition in the vapor space of the tank. The DAS collected required information during the testing. Seven data packages were issued during the performance of PVT-1 containing data from the DAS and data collected manually by High Level Waste Operations (HLWO). The manual data was on the parameters of interest as outlined in the Test Plan (Ref. 9.5) and collected from the instruments listed on the "Instrument List and Calibration Status for the ITP Process Verification Tests (U)" (Ref. 9.6).

Samples were pulled from Tank 48 using the Variable Depth Sampler (VDS) and dip sampling at various times for the duration of the test. The samples were analyzed for several constituents including Cs-137 concentration, NaTPB, potassium, soluble copper, and NaTPB degradation products as outlined in the Test Plan. (Ref. 9.5)

3.2 Gas Chromatographs and Data Acquisition System Data

The data obtained by the GC DAS has been compiled into a series of reports that have an operations/test sequence, a GC DAS Plot List, and plots of all the data for various time frames during the test. Listed below are the reports and the time frame they cover. (Ref. 9.7)

Report 1 - HLW-ITP-960266	10-31-96 0935 Hours to 11-4-96 1035 Hours. Initial samples and NaTPB addition to Tk 48.

Report 2 - HLW-ITP-960267	11-4-96 1000 Hours to 11-11-96 1000 Hours. 2nd post strike samples pulled.
Report 3 - HLW-ITP-960268	11-11-96 0935 Hours to 11-18-96 0930 Hours. 3rd and 4th post strike samples pulled.
Report 4 - HLW-ITP-960269	11-18-96 0930 Hours to 11-25-96 0930 Hours. Filtrate production, IW flush of filter, caustic lay-up of filter, and 1st post filter samples pulled.
Report 5 - HLW-ITP-960270	11-25-96 1000 Hours to 12-2-96 1000 Hours. 2nd post filter sample pulled.
Report 6 - HLW-ITP-960271	12-2-96 1000 Hours to 12-9-96 1000 Hours. Chem clean/filter flushed (2770 gals. of water into Tk48), post chem clean sample pulled.
Report 7 - HLW-ITP-960272	12-9-96 1000 Hours to 12-16-96 1000 Hours. Column and filter drain to Tk 48 after flush, 1st weekly sample pulled.

3.3 Test Data Evaluation

Analytical results for the PVT-1 samples are listed in Table 1.

3.3.1 Cs Precipitation

A requirement of the ITP process is the ability to precipitate Cs-137 and maintain decontamination long enough to complete filtration steps. Although the test plan for PVT-1 had indicated a Cs-137 concentration requirement of 85 nCi/g or less following precipitation, a change in the Z Area ALARA (As Low As Reasonably Achievable) guide has reduced the limit to 35 nCi/g. The Cs-137 precipitation was successful. The predicted Cs-137 concentration after NaTPB addition was 1-12 nCi/g. The measured concentration was 2-8 nCi/g.

Changes in the Cs-137 concentration in Tank 48 during the PVT-1 test are shown in Figure 1. Decontamination (Cs-137 < 35 nCi/g) was maintained for 22 days (528 hours). The predicted duration was 18-20 days (Ref. 9.1).

The NaTPB concentration in Tank 48 was 60 mg/L immediately after the precipitation. The calculated expected concentration from Reference 1 was 202 mg/L based on the sample results, tank volume and expected NaTPB addition at the time the document was written (September 18, 1996). The actual tank composition and volume changed significantly by the time the test was started on November 3, 1996. The table below provides a comparison of the calculated TPB concentration versus the actual values seen in Tank 48. The calculated values have been corrected for the conditions that were present just prior to beginning PVT-1. In addition, the proposed flow sheet values are shown for comparison.

Comparison of TPB in Tank 48

	Calculated Expected Amounts in Tank 48	Actual Amounts Accounted for in Tank 48	Proposed * Flow Sheet
Total NaTPB Added (kg)	218.5	218.5	11,962
Stoichiometric amount of NaTPB required to precipitate K^+ (kg)	105.5	105.5	10,874
Excess NaTPB Added (kg)	113	54	1,088
Concentration of Excess NaTPB (mg/L)	128	60	479

* *Proposed flow sheet values based on a 10 % stoichiometric excess, 0.014 M K^+ concentration, and a 600,000 gallon batch size.*

As can be seen from the above table, a discrepancy exists between the expected concentration of NaTPB in solution versus what was actually observed in Tank 48. This discrepancy leaves approximately 59 kg of NaTPB unaccounted for in PVT-1. This discrepancy is larger than expected based on analytical errors but agrees with similar bias observed in laboratory tests. The cause is being investigated (Ref. 9.8) by the Savannah River Technology Center (SRTC).

3.3.2 Decomposition Rate of NaTPB

An understanding of the decomposition of NaTPB to intermediate organic products and benzene is required to finalize the Authorization Basis for ITP operations and associated safety equipment and controls.

The rate of loss of NaTPB and the changes in concentrations of the intermediates 3PB, 2PB, and 1PB and one decomposition product (phenol) were successfully measured. The loss of NaTPB is shown in Figure 2 and the changes in the intermediates and product are shown in Figures 3 to 6.

The expected loss of NaTPB was predicted prior to the test (Ref. 9.1) based on a simple exponential rate expression ($C_{TPB} = C^{TPB}_0 e^{-kt}$ where C^{TPB}_0 is initial TPB^- concentration) using a rate constant (k = 0.00335 hr-1) derived from laboratory tests at 40 °C. The tank rate was expected to fall within the

range 0.00067 to 0.0168 hr-1. Figure 2 compares the model predictions to the results from PVT-1.

Prior to the test, it was anticipated that the small amount of NaTPB added to the tank would not decompose rapidly enough to produce significant trends in the concentrations of the intermediates and products. Therefore, no time-dependent predictions of the changes were made. However, bounding predictions were made assuming that all of the excess NaTPB decomposed rapidly to a single product
(Ref. 9.1). A change larger than the bounding predictions would indicate that more tetraphenylborate than was added at the start of the test had decomposed (possibly signifying decomposition of the solid KTPB). During the test, small trends in the intermediates were measured and are discussed below. The observed changes are compared to revised predictions based on the amount of NaTPB and intermediates actually measured at the start of the test.

The concentration of 3PB was 42 mg/L at the start of the test and peaked at 57 mg/L before it began a slow decline (Figure 3). Thus, it did not exceed the pretest prediction of 194 mg/L (Ref. 9.1) or the corrected prediction of 84 mg/L (based on actual tank starting composition). The peak was lower than the predicted limit because the NaTPB decomposed more slowly than assumed in the prediction, allowing time for the 3PB to decompose to other products.

The concentration of 2PB increased gradually during the test, starting at 20 mg/ L and ending at 47 mg/L (Figure 4). Thus, 2PB did not exceed the pretest prediction of 107 mg/L (Ref. 9.1) or the corrected prediction of 52 mg/L (based on actual tank starting composition). The 2PB did not reach the predicted peak concentration because other products were formed.

The concentration of 1PB slowly decreased during the test, dropping below the analytical detection limit after 800 hours (Figure 5). Thus, it did not exceed the pretest prediction of 120 mg/L (Ref. 9.1) or the corrected prediction of 51 mg/L (based on actual tank starting composition). It appears that 1PB did not increase because of the slow decomposition of the NaTPB, 3PB, and 2PB.

The phenol concentration did not change significantly (Figure 6). The initial concentration was 1.19±.11 g/L and during the test it averaged 1.18±.07 g/L with no significant trend up or down. The expected yield of 10 % would have increased the phenol by only 7 mg/L (based on decomposition of 61 mg/L of NaTPB). Therefore, no conclusion about the yield of phenol can be drawn from the data.

3.3.3 Benzene Mass Transfer

Understanding the rate at which benzene can be released from the slurry into the vapor space and the effects of slurry pump operation on this rate is key to establishing the basis for safe operation of ITP. Measurements were made during PVT-1 to determine if benzene concentrations in the vapor space ever exceeded the predicted values, which could call for review of the assumptions being used in Authorization Basis development.

The mass transfer calculations employed in developing these estimates relied upon conservative mass transfer coefficients and benzene generation rates to estimate vapor space concentrations during PVT-1. A more complete description of the values employed in the development of these estimates can be found in Reference 9.2.

During PVT-1, benzene in the Tank 48 vapor space did not exceed 10 ppm (versus LFL =13,000 ppm). Prior to the start of PVT-1, a number of conservative estimates were made of the expected vapor space concentration that would be reached in Tank 48 (Ref. 9.2). The lowest of these conservative estimates predicted a maximum benzene concentration of 120 ppm. The lower measured benzene concentration in Tank 48 is not unexpected based on the conservative assumptions used in this prediction including:

- A higher than measured soluble TPB concentration (128 mg/L used in prediction vs. 60 mg/L measured in Tank 48)
- A higher than measured soluble 1PB concentration (131 mg/L used in prediction vs. 30 mg/L measured in Tank 48)
- Faster reaction kinetics for the degradation of triphenylboron and diphenylboric acid (instantaneous versus non-instantaneous as indicated from PVT-1 sample results)
- Faster tetraphenylborate decomposition than measured in Tank 48

These results indicate that a significantly lower benzene source term existed in Tank 48 during PVT-1 than was anticipated from predictions. Thus, based on this lower source term, it was expected that the observed benzene concentrations in the vapor space would be significantly lower than predicted.

Similar assumptions were employed in predicting releases from Tank 50 during PVT-1. Thus, it was expected that benzene would be below detectable levels in the Tank 50 vapor space in the measurements that were made.

Since all benzene measurements were lower than predicted, the PVT-1 results did not challenge the assumption that the current mass transfer models may be used to bound Tank 48 and Tank 50 behavior.

3.3.4 Filter Performance

The filter was not operated at the conditions required to adequately assess filter performance. The filter operated well within normal operating parameters. No degradation in filter performance was observed for the operating conditions of the test (approximately 4 psi delta p at 20 gpm filtrate flow rate).

3.3.5 Filter Cleaning by Oxalic Acid Addition

Demonstration of the filter cleaning procedure was required to address both safety and operational issues. Oxalic acid is known to cause decomposition of TPB, which will lead to increased benzene production. It was predicted that the addition of oxalic acid during filter cleaning would not cause a significant change in benzene production due to the rapid neutralization of the acid by the high hydroxide waste. This prediction was tested during PVT-1. In addition, the filter cleaning procedure was demonstrated in the field.

The impact of adding oxalic acid to Tank 48 was also determined during the filter cleaning operations. As predicted, no changes in benzene vapor concentration occurred and no unanticipated changes in the Cs-137 or TPB concentration occurred. There were no detectable changes in the nitrosobenzene or nitrobenzene concentrations in the slurry. The vapor space showed no detectable nitrobenzene and only a trace of nitrosobenzene (~1.4 ppm).

The test verified that the oxalic acid added during filter cleaning overwhelmingly reacts with the hydroxide in Tank 48 resulting in little or no TPB decomposition.

3.3.6 Tributyl Phosphate Resolution

In the Safety Evaluation Report (SER) for the In Tank Precipitation (ITP) Process Verification Test 1 (PVT-1) (Ref. 9.9), an issue was raised pertaining to the effect of tri-n-butyl phosphate (TBP) on the rate of release of benzene from Tank 50. ITP engineering report, HLW-ITP-960328, "Effect of TBP on Tank 50 Benzene Release Rate During PVT-1 (U)", October 8, 1996, and its associated Technical Review and Unreviewed Safety Question screening determined there was no impact of adding the TBP to Tank 50 during PVT-1.

3.3.7 Sampling

All sampling and analyses were completed as required by the test plan. The analytical results are given in Table 1. A complete report of the results with the quality assurance measures has been issued by SRTC (Ref. 9.10).

The uncertainties noted in Table 1 reflect the variability observed in the duplicate samples taken and tested for each time point. The uncertainty should include analytical method and instrument uncertainties as well as any local spatial variability of the material in the tank. Since pumps were run prior to each sampling event, it is reasonable to extrapolate the measurements obtained at the sampling point to the entire tank contents without assuming significant additional spatial variability.

Tank 48 was sampled eleven times, including the pre-strike sample. Each filtrate hold tank (FHT) was sampled once, and Tank 50 was sampled twice (before and after the FHT's were transferred). Each time Tank 48 was sampled, two 100-mL bottles were filled. The FHT and Tank 50 samples were larger (500 mL) and only one bottle was used. A blank sample containing distilled water was created at each sampling event. The blanks were transported and analyzed along with the tank samples for quality assurance. Although the blank samples are obvious from the analytical results, they are indicated in the "Source" column in Table 1.

In two instances, there was insufficient sample to complete the analysis for insoluble solids. Both prestrike samples were consumed by the analyses, so insoluble solids were measured on the first post-strike samples. The first post-filtration samples were also supposed to be analyzed for insoluble solids. One of these (ITP-403) did not contain sufficient material to complete the analysis. Therefore, the other sample taken at the same time (ITP-404) was analyzed in duplicate, providing the results.

Three sample bottles were found to be dilute relative to their duplicates. One of the first post-strike sample pair (ITP-387), one of the first weekly sample pair (ITP-417), and one of the second weekly sample pair (ITP-428) were more dilute than their twin by 25, 33, and 22% respectively. This is believed to have occurred during operation of the Variable Depth Sampler (VDS). The exclusion of the results from these three samples does not significantly impact any of the test objectives. Plans to procure and install a new tank sampler are underway.

One sample set was taken via dip sampling rather than the VDS sampler. These were the third post-strike samples (ITP-392 and ITP-393). The results for the dip bottles do not differ significantly from samples taken by the VDS as evidenced by the results obtained.

3.4 Accomplishments / Conclusions of PVT-1 Testing

PVT-1 was successful in meeting its objectives. The accomplishments and conclusions from the PVT-1 testing are shown below:

- Cesium precipitation was obtained and maintained with 60 mg/L measured soluble TPB remaining after precipitation. The length of time that decontamination was maintained was adequate to support the planned flow sheet reaction/concentration cycle. In addition, after the excess TPB was decomposed, the Cs-137 buildup returned to the pre-PVT-1 rate of approximately 9 nCi/g per day.

- No rapid decomposition of TPB was observed, and decomposition intermediates were successfully tracked throughout the test. The formation of the decomposition intermediates was well within the bounding model predictions. In addition, the PVT-1 data set will be used for verification of the models being developed as a part of the chemistry program outlined in the DNFSB Recommendation 96-1 response plan.

- Since all benzene measurements were lower than predicted, the PVT-1 results did not challenge the assumption that the current mass transfer models may be used to bound Tank 48 behavior. However, since all benzene vapor space measurements were less than 10 ppm, no conclusions about the exact accuracy of the mass transfer model can be made.

- The filter was not operated at the conditions to adequately assess filter performance. However, the filter operated well within normal operating parameters, and no degradation in filter performance was observed at the operating conditions of the test.

- Benzene generation was monitored during oxalic acid cleaning, and the addition of oxalic acid was shown not to present a benzene generation concern. Since the filter did not indicate any evidence of degradation, filter cleaning was not demonstrated, however, the procedures for cleaning were successfully demonstrated in the field for the first time.

Overall, the process met predictions and expectations.

4.0 SPECIAL EQUIPMENT USED

Special instrumentation in the form of Gas Chromatographs with a Data Acquisition System was connected to two "instrument trees" inserted into the Tank 48 vapor space. The instrument trees enabled the analysis of localized vapor composition in the vapor space of the Tank. The DAS collected information on a continuous basis during the testing. Data management was governed by the "ITP Process Verification Test (PVT) Desktop Procedure for Data Acquisition in the DAS Hut on Tank 48 (U)". (Ref. 9.11)

5.0 ACCEPTANCE CRITERIA

The PVT-1 Test Plan indicated a single criterion for the test: Demonstrate the capability to re-precipitate Cs-137 in Tank 48 to a level that meets filtrate process requirements of less than 85 nCi/gram for transfer to Tank 50.

As noted above, changes in the requirements since initiation of PVT-1 have reduced the limit for filtrate from 85 nCi/g to 35 nCi/g. Both the stated test acceptance criterion and the more stringent limit were met. The actual concentration of Cs-137 after TPB addition was 2-8 nCi/g, and the filtrate was maintained below 35 nCi/g for more than 22 days.

6.0 PROCEDURE CHANGES

SW16.2-IOP-CONC, Rev 3, CONCENTRATION (U)

This procedure had 9 Immediate Procedure Changes (IPC) written, approved, and incorporated during the performance of the test. Listed below is a short summary of each IPC.

IPC 962118-ITP - Approved 10-29-96

This IPC was written to incorporate the changes needed in the IOP to meet the intent of the Test Plan for PVT-1.

Added Appendix 7.2 with sample analysis requirements
Added attachment 8.3, tank 48 PVT-1 sampling
Added attachment 8.7 Tank 48 SRTC Grab Sample
Deleted section 3.2 note about prerequisites and steps about waste additions to the tank and sampling feed tanks to Tank 48
Deleted Chem Addition spoolpiece installation at B3 riser.
Added step to have Doorstops available for sample transport.
Added step to route analyzer exhaust to atmosphere
Added verification waste transfer system operable.
Deleted section 4.1.3, Concentration Prestart Operation.
Added step to sample NaTPB drums.
Deleted steps to calculate additions to Tank 48.

Deleted steps to transfer salt feed into the tank and add chemicals and dilution water.
Modified step to monitor benzene depletion and temporary shutdown of slurry pumps.
Modified step for Non-routine sampling per appendix 2.
Deleted steps on pre-reaction samples and dilution water additions.
Deleted steps on Sodium Titanate (ST) additions.
Added steps on NaTPB addition to Tank 48.
Changed pump run time to 16 hours after NaTPB addition.
Added steps to obtain samples within 2 hours of pump shutdown.
Added attachment 3 on sampling.
Added step to sample Tank 50.
Changed step to select hold tank 1.
Added step to only fill 2 hold tanks.
Added step for normal shutdown after 2 hold tanks filled.
Added steps to delete using deionized water to caustic dumpster.
Added steps about hold tank transfer to Tank 50.
Modified hold tank Hi level setpoint.
Modified step to ensure less than the equivalent amount of 300 gallons of 0.57 M NaTPB was added.

IPC 962149-ITP - Approved 11-1-96

This IPC was written to tighten the controls on the amount of NaTPB to be added and allow the test to start with Tank 48 temperature less than 40 degrees C. The changes had no impact on the test results.

Added precautions to limit amount of NaTPB added, maintain Tank 48 temperature less than 40 degrees C, limit Tank 48 breaches, slurry pumps to be operated to control flammable mixtures in the vapor space, and give Mode B as the preferred ventilation mode.

IPC 962217-ITP - Approved 11-11-96

This IPC was written because the 240 hour samples could not be pulled due to problems with the VDS. A set of samples were pulled by dip sampling to complete sampling before the start of concentration. The missed set of samples had no affect on the test results.

Deleted 240 hour post NaTPB sample.

IPC 962227-ITP - Approved 11-12-96

This IPC was written because it had been greater than 30 days since Tank 50 had been sampled. A base line sample was required, it was determined the previous sample would provide the information need.

Deleted requirement to sample Tank 50 within 30 days before adding

NaTPB.

IPC 962244-ITP - Approved 11-14-96

This IPC added detailed information required for pulling samples and changed the steps for pulling dip samples. Changes had no impact on the test results.

Added steps to perform Tank 48 sampling following Chem. Cleaning.

IPC 962321-ITP - Approved 11-21-96

This IPC was written to allow leak testing of the backpulse system. It had no impact on test results.

Added steps for performing backpulse operation.

IPC 962336-ITP - Approved 11-22-96

This IPC was added to ensure slurry pumps were operating for sampling that was added per IPC 962244.

Added step to ensure all slurry pumps operating.
Added step to stop slurry pumps after 4 hours.

IPC 962386-ITP - Approved 12-1-96

This IPC was written to allow continued testing without performing a surveillance because all the requirements were not meet by this testing. No impact on the test results.

Changed step to "IF" precipitation cycle completed then perform a surveillance.

IPC 962417-ITP - Approved 12-4-96

This IPC was written to delete the additional sampling added by IPC 962244. No impact on the test results.

Deleted steps to sample Tank 48.

SW16.1-SOP-96H(CC), Rev 1, Chemical Cleaning (U)

This procedure had 3 Immediate Procedure Changes (IPC) written, approved, and incorporated during the performance of the test. Listed below is a short summary of each IPC.

IPC 962221-ITP - Approved 11-20-96

This IPC was written to ensure at least one GC was in service during Chem Clean and deleted steps to hook up hose that would not be used. No impact on test results.

Deleted step to install hose from DI water to caustic dumpster.
Added step to verify Gas Chromatography in service.

IPC 962416-ITP - Approved 12-4-96

This IPC was written to ensure all samples requested by HLWE were obtained. No impact on test results, obtained additional information.

Deleted steps to stop slurry pumps 12 hours after OA addition.
Added steps to stop and start slurry pumps.
Added step to record benzene concentration.
Added steps for Tank 48 liquid and vapor space samples.

IPC 962445-ITP - Approved 12-7-96

This IPC was written to allow the selection of caustic pumps to be used to fill the system. No impact on the test results.

Added steps to line up the selected caustic pump.

7.0 NON-CONFORMANCE REPORTS

No NCR's were written during this test.

8.0 ATTACHMENTS

Table I - SRTC PVT-1 Sample Results

Figure 1 - Cs-137 Concentration

Figure 2 - NaTPB Concentrations During PVT-1

Figure 3 - 3PB Concentrations During PVT-1

Figure 4 - 2PB Concentrations During PVT-1

Figure 5 - 1PB Concentrations During PVT-1

Figure 6 - Phenol Concentrations During PVT-1

9.0 REFERENCES

9.1 D. D. Walker, "Expected Response following addition of NaTPB to Tank 48 (U)", **SRT-LWP-96-0096**, September 18, 1996

9.2 R. A. Peterson & R. F. Swingle, Predictions of Tank 48 and Tank 50 Benzene

Concentrations During PVT-1, **WSRC-TR-96-0257**, August 19, 1996

9.3 D. D. Walker & C. A. Nash, "Results From Tank 48 Slurry Decontamination And Decomposition Experiments In Support of ITP Process Verification Testing (U), **WSRC-TR-96-0190**, September 6. 1996

9.4 Safety Evaluation for In-Tank Precipitation Initial Process Verification Testing (U), **HLW-REG-960090**, August 1996

9.5 In-Tank Precipitation Plan for Process Verification Test, Phase 1,**HLW-ITP-960247, Rev 1**

9.6 Instrument List and Calibration Status for the ITP Process Verification Tests (U), **HLW-ITP-960261, Rev 3**

9.7 GAS CHROMATOGRAPHY / DAS DATA REPORTS

Report 1 - **HLW-ITP-960266** 10-31-96 0935 Hours to 11-4-96 1035 Hours

Report 2 - **HLW-ITP-960267** 11-4-96 1000 Hours to 11-11-96 1000 Hours

Report 3 - **HLW-ITP-960268** 11-11-96 0935 Hours to 11-18-96 0930 Hours

Report 4 - **HLW-ITP-960269** 11-18-96 0930 Hours to 11-25-96 0930 Hours

Report 5 - **HLW-ITP-960270** 11-25-96 1000 Hours to 12-2-96 1000 Hours

Report 6 - **HLW-ITP-960271** 12-2-96 1000 Hours to 12-9-96 1000 Hours

Report 7 - **HLW-ITP-960272** 12-9-96 1000 Hours to 12-16-96 1000 Hours

9.8 Technical Task Plan for Solids Stability Studies of Tetraphenylborate Slurries (U), **WSRC-RP-96-602, Rev 1**

9.9 In-Tank Precipitation Safety Evaluation Report (SER), Rev 2, Supplement 7, Safety Evaluation (SE) for Initial Process Verification Testing (PVT)

9.10 D. D. Walker, et al, "Analytical Results for Samples from Process Verification Test, Phase 1 (U)", **WSRC-TR-97-0041, Rev. 0,** February 21, 1997

9.11 ITP Process Verification Test (PVT) Desktop Procedure for Data Acquisition in the DAS Hut on Tank 48 (U), **HLW-ITP-960088**, May 15, 1996

APPENDIX A - CHRONOLOGY OF TEST SEQUENCE

PVT-1 testing started on 10-30-96 with the start of SW16.2-IOP-CONC, Rev 3, "Concentration (U)" procedure. Immediate Procedure Change (IPC) 962118-ITP modified the procedure to allow the NaTPB addition and added the required monitoring and sampling to meet the requirements in HLW-ITP-960247, Rev 1, "In-Tank Precipitation Plan For Process Verification Test, Phase 1 (U)".

All slurry pumps in Tank 48 were started and brought up to speed by 1634 on 10-31-96 after resolving problems with bearing water during their startup. The pumps were shutdown on 10-31-96 at 2306 when it was recognized that the hydrogen to benzene ratio was outside of the values used in the Authorization Basis. Since the amounts of hydrogen and benzene involved were so small, tank 48 was at all times in a safe condition. An Authorization Basis change was made (HLW-CRF-96059 to AB Document HLW-REG-960090) and approved. On 11-1-96 permission was given to start the pumps. The pumps were backup to speed on 11-2-96 at 1230. The pumps ran until 0145, 11-3-96, when they were stopped to draw the initial sample (pre-addition sample) of Tank 48. The pumps were again started by 0602 and the addition of 288 gallons of NaTPB made between 1015 and 1235 on 11-3-96. (NOTE: No increase in tank vapor space benzene was noted during the addition.)

The first set of post reaction samples were pulled after the pumps were stopped at 0439 on 11-4-96. Sampling was completed at 0615.

All slurry pumps were started and brought up to speed between 0609 and 0650 on 11-6-96 and were allowed to run until 1313. The second set of post reaction samples were drawn by 1518.

All slurry pumps were started and brought up to speed by 2225 on 11-8-96 and allowed to run until 0442 on 11-9-96. The attempt to pull the first sample was stopped by failure of the VDS (shear pin broke on hand crank). Work requests were generated for the repair of the VDS and an IPC written to delete one of the remaining samples before the start of filtrate production. The third set of samples were pulled as dip (grab) samples and the sampling was completed at 0345 on 11-12-96.

Steps were started on 11-13-96 at 0105 to start filtrate production. The demister spray rotometer was found broken at 0335 and repaired by 1624. At 1729 the procedure stopped when problems with the column filling were encountered. The procedure was continued at 2058 and the nitrogen heaters energized. The heaters tripped off at 2119 and trouble shooting started. The problem was thought to be excessive load due to the cold temperatures. The heaters were re-energized at 0135 on 11-14-96.

At 1700 on 11-14-96, a filter feed pump problem was identified with oil leaking from the pump, and trouble shooting on the nitrogen heaters started again. The test procedure was stopped for this repair work. The filter feed pump motor was replaced, and the mother board in the nitrogen heater control panel was changed.

A shift briefing was held and filtrate production started at 2353 on 11-19-96. Production stopped at 0204 on 11-20-96 due to loss of nitrogen stripping gas flow. The loss of nitrogen flow was caused by maintenance doing trouble shooting on the column recirculation valve that was not responding correctly. Production started again at 0630. Hold tank # 1 was filled at 1344 and output shifted to hold tank # 2. Hold tank # 2 was filled and production stopped at 2255. Hold Tank sample results were satisfactory for transfer to Tank 50. Operations attempted a backpulse on the filter but a leak was identified on the backpulse chamber fill line. The leak was repaired, but the next attempt did not work due to valve 24 malfunctions.

After repairs, a successful backpulse was completed at 0149 on 11-22-96. The attempt of a second backpulse failed due to valve 24 problems again. Management made the decision to continue the procedure to drain, flush, and place Filter 2 in Inhibited Water (IW) lay-up. The filter feed pump was stopped at 0506 on 11-22-96. Repairs to valve 24 on the backpulse chamber were addressed by Work Package BNJJH.

Filter drain and flushing with IW was completed on 11-22-96 and the filter placed in caustic lay-up on 11-23-96.

All slurry pumps were started at 1557 on 11-24-96 and run until 2210. Sampling with the VDS was completed at 2316.

On 11-25-96 hold tanks 1 and 2 were transferred into Tank 50 at 1800. Dip samples of Tank 50 were pulled before and after the transfer.

On 11-30-96 all slurry pumps were started by 1752 and ran until 0049 on 12-1-96. Samples were pulled from tank 48 by 0210.

SW16.1-SOP-96H(CC)-1, Rev 1, "Chemical Cleaning (U)", procedure was started on 12-2-96 at 0911. During the course of the day, the filter was filled and drained three times with deionized water.

The 1000 gpm flush of the filter was performed on 12-4-96 and two more fill and drains were done after the flush. All slurry pumps were started by 2353 in preparation of the oxalic acid dump into the tank.

Filter 2 was placed in the OA 2 hour soak at 0013 on 12-5-96. The filter drain to tank 48 was started at 0214 and completed at 0225. No benzene was detected by

the GC DAS by 0425. The grab sample for SRTC was pulled from tank 48 at 0515. Slurry pumps were stopped at 0912 and VDS samples pulled by 1015. Fills and drains of the filter with DI water completed at 1543.

The high volume flush (1000 gpm) of the filter was completed at 1353 on 12-6-96. Two filter fills and drains were completed at 2345.

The filter was filled with caustic at 0250 on 12-7-96 and drained at 0450 after a 2 hour soak. The filter was re-filled with caustic by 0543, drained and filled with caustic a third time at 0847. A partial drain and fill with DI water was completed at 1330 (DI and caustic mix in filter).

The filter was placed in caustic lay-up on 12-11-96 at 1500.

The slurry pumps were started by 0830 on 12-16-96 and stopped at 1018 for sampling. Problems with the VDS delayed sampling on the first sample until 1715 and the second sample until 2251.

SRTC requested additional samples of Tank 48 for follow-up after those drawn on 12-16-96. Samples have been pulled on 12-30-96, 1-13-97, and 2-8-97. Additional samples will likely be pulled every 4-6 weeks for routine monitoring of tank 48 chemistry not associated with PVT-1.

[TO OBTAIN HARDCOPIES OF TABLES AND FIGURES, CALL 202-586-3887]

TABLE I

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6