DEFENSE NUCLEAR FACILITIES SAFETY BOARD

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October 9, 1997

The Honorable Alvin L. Alm
Assistant Secretary for Environmental Management
Department of Energy
Washington, D.C. 20585

Dear Mr. Aim:

Defense Nuclear Facilities Safety Board (Board) staff review teams have visited the Savannah River Site several times this year to review implementation of Recommendation 96-1 at the In-Tank Precipitation (ITP) Facility, and to assess the authorization basis and safety programs for the high-level waste tank farms. The Board requested Mr. R. Tontodonato of the Board's staff to review the reports of these visits and to summarize these findings for us. The enclosed report is his summary of the issues identified during each site visit and the progress made in resolving each open item.

There are several key issues the Board would like to draw to your attention. The numerous observations made by our staff regarding the ITP nitrogen inerting systems make it clear that great care must be taken to ensure these systems are rigorously effective and reliable. Furthermore, the staffs observations regarding controls on ITP pump operations highlight the fact that ITP appears to be developing an undue reliance on administrative controls. Engineered controls would be preferable, to the extent that they are practical, for a facility facing such a long and technically demanding mission. Finally, the prolonged discussions that have taken place regarding the accident analyses and controls for hydrogen deflagrations in waste tanks and waste tank overheating indicate that closure of these issues is proving difficult and may warrant increased scrutiny from the Department of Energy. The Board is closely following the progress of the research on the chemistry of the ITP process, and the results that continue to come in with bearing on the safety of the process.

The enclosed reports provide a synopsis of the observations made during the reviews conducted by the Board's staff and are forwarded for your consideration. If you have any questions, please feel free to call me.

Sincerely,

John T. Conway
Chairman

c: Mr. Mark Whitaker

Enclosures

DEFENSE NUCLEAR FACILITIES SAFETY BOARD

April 15, 1997

MEMORANDUM FOR: G. W. Cunningham, Technical Director

COPIES: Board Members

FROM: D. Drop
R. Tontodonato

SUBJECT: Review of Savannah River Site In-Tank Precipitation Facility, April 2–3, 1997

1. Purpose

This report documents a visit by Defense Nuclear Facilities Safety Board (Board) staff members D. Drop, D. Napolitano, and R. Tontodonato to the Savannah River Site (SRS) on April 2–3, 1997. The purpose of this visit was to review the implementation of Board Recommendation 96-1 regarding process safety at the In-Tank Precipitation (ITP) Facility.

2. Summary

ITP Equipment Upgrades. Several equipment upgrades are currently being installed at ITP. Insulation is being installed on the exhaust systems and instrument air lines for Tanks 48 and 49 to improve cold-weather reliability, instrument air will be replaced with dry nitrogen, and a new safety-class backup nitrogen system is being constructed. A new pipeline is being constructed for transfers from Tank 49 to Tank 48, to bypass transfer facilities shared with non-ITP tanks. Westinghouse Savannah River Company (WSRC) plans to replace the manually operated variable-depth sampler in Tank 48 with a fluidic diode sampling system that can draw samples without opening a tank riser.

Tank 48 Vapor Space Mixing. Based on operational data, WSRC believes the Tank 48 vapor space is well mixed both during normal operations with a nitrogen purge flow and during standby conditions when the purge is lost. Computational fluid dynamics modeling will be used to assess further whether this is true for the normal operational mode, but not for loss-of-ventilation conditions. The Board staff is concerned that the data obtained during loss-of-ventilation conditions (1) may not be representative of the entire vapor space, and (2) may not have been taken under bounding temperature conditions.

ITP Chemistry Program. WSRC has made significant progress in understanding the chemistry associated with the ITP process. Initial results show that copper, organic compounds, dissolved oxygen, and noble metals all play a role in the decomposition of soluble tetraphenylborate and its degradation products. Progress has also been made in understanding how benzene is retained in the ITP slurry. Further testing in both areas is planned.

3. Background

Board Recommendation 96-1, issued on August 14, 1996, recommends that the Department of Energy (DOE) not proceed with large-scale process testing at ITP until the mechanisms for benzene generation, retention, and release are better understood, and adequate safety measures to prevent benzene deflagrations have been developed. DOE's implementation plan for this recommendation, transmitted to the Board on November 12, 1996, commits to conducting a testing program that will develop an improved understanding of ITP chemistry and appropriate process controls. The Board staff conducted reviews at SRS to assess the implementation of Recommendation 96-1 in December 1996 and January 1997. The key issues discussed during these reviews were the need for improving the reliability of the Tank 48 ventilation system, and the safety strategy and technical basis for future ITP operations.

4. Discussion

During the site visit, the Board staff discussed DOE's progress in implementing Recommendation 96-1, including equipment upgrades planned for ITP, investigations into vapor space mixing in Tank 48, progress in the ITP chemistry program, and the reliability of tank cooling systems. Key observations in these areas are summarized below.

ITP Equipment Upgrades. WSRC is installing several equipment upgrades to improve the ventilation system reliability for Tanks 48 and 49, and to improve and simplify ITP operations. Since about half the ventilation outages in the past year were attributed to cold weather, insulation and heat tracing have been installed on exhaust and instrument air lines on Tank 48. WSRC also plans to supply instrument air lines with dry nitrogen to avoid condensation and freezing. Similar upgrades will be installed on Tank 49. Additionally, WSRC is attempting to identify and correct vulnerabilities in ITP's electrical system, such as single circuit breakers supplying power to an excessive number of unrelated components.

Several new systems are also being installed. Construction of the new safety-grade backup nitrogen system is under way. In addition, a new pipeline is being constructed for transfers from Tank 49 to Tank 48, to bypass transfer facilities shared with non-ITP tanks. Lastly, WSRC plans to replace the manually operated variable-depth sampler in Tank 48 with a fluidic diode sampling system that can draw samples without opening a tank riser.

Tank 48 Vapor Space Mixing. One of the key assumptions of the ITP safety strategy is that mixing of nitrogen, oxygen, and benzene in the Tank 48 vapor space is adequate to prevent localized flammable mixtures from forming. Furthermore, it is important that measurements of oxygen and benzene concentrations be representative of the entire vapor space, since the planned Technical Safety Requirements will require maintaining those concentrations below specified levels. WSRC is working to validate the assumption of a well-mixed vapor space for both the normal operating mode and loss-of-ventilation conditions. Experimental data were taken by two oxygen analyzers and two gas chromatograph poles at two radial positions in Tank 48 during both modes of operation. These data show little difference in gas composition at the different locations measured. WSRC is currently documenting these experiments and drafting a report summarizing relevant vapor space mixing calculations. Work that remains to be done and Board staff comments are summarized below.

Normal Operating Mode—WSRC will use steady-state computational fluid dynamics modeling to verify that the data obtained during the normal operating mode in Tank 48 are representative of the entire vapor space. These calculations include steady-state results from the COMPACT-3D computer code, used in 1995 to model the forced convective flow in Tank 48. This code did not model transient effects well (e.g., it predicted that residual momentum effects would persist to a limited degree for 3 days after the purge flow had been shut off), but WSRC believes the steady-state results are valid. The COMPACT-3D results will be verified by FLUENT, another computational fluid dynamics code.

Loss-of-Ventilation Conditions—WSRC believes that the available data, representing air in-leakage rates ranging from the expected low range to very high rates, adequately demonstrate that the vapor space remains well mixed during loss-of-ventilation conditions. WSRC does not plan to verify by calculations (e.g., with computational fluid dynamics modeling) that the data are representative of the entire vapor space. It is not clear how WSRC plans to determine whether there is a potential for poorly mixed regions to form in uninstrumented regions of the tank.

Furthermore, it is not clear that these measurements were taken during worst-case conditions for mixing. Based on the reported tank dome and liquid temperatures, the loss-of-ventilation test data appear to have been taken during conditions favorable to natural convective mixing. It is possible that mixing would be less complete during periods less conducive to natural convection (e.g., temperature inversions where the tank top is warmer than the waste surface). The potential for temperature inversions in Tank 48 has not been evaluated, and such events could become more likely if WSRC decides to maintain a lower waste temperature to minimize tetraphenylborate decomposition rates. It would be prudent to obtain a better understanding of vapor space mixing during loss-of-ventilation conditions, especially during worst-case temperature conditions. It could then be determined under what conditions oxygen and benzene measurements will be representative of the entire vapor space and whether there may be conditions where these measurements will not be representative.

ITP Chemistry Program. The Savannah River Technology Center (SRTC) has made significant progress in the ITP chemistry program. The status of the test program is summarized below.

Tetraphenylborate Decomposition—Initial test results show that copper, organics, dissolved oxygen, and noble metals all play a role in the catalytic decomposition of soluble tetraphenylborate and its degradation products. Dissolved oxygen appears to act by affecting the oxidation state of the copper catalyst, and it may affect other catalysts as well. Copper exists as Cu(II) in an oxygen-rich (aerobic) environment, whereas it takes the form of Cu(I) in an oxygen-deficient (anaerobic) environment. The current data suggest that Cu(I) is an important catalyst in the decomposition of soluble tetraphenylborate. However, Cu(I) catalysis alone does not explain the tetraphenylborate decomposition rates observed in Tank 48; other constituents, most likely noble metals and organics, are also catalyzing decomposition processes.

Similarly, Cu(I) catalysis alone does not explain the maximum decomposition rates observed for the degradation products of tetraphenylborate. SRTC believes the observed rate for triphenylborane adduct may be a result of either (1) increased salt/hydroxide concentrations (which have been observed to increase decomposition rates) or (2) an unidentified alternate catalyst. Cu(II) appears to be the key catalyst for both diphenylboronic acid and phenylboronic acid decomposition.

The effects of dissolved oxygen, as well as those of organics and other suspected catalysts, will continue to be studied in a set of statistically designed catalyst identification tests. Constituents no longer suspected of being catalysts will be included in these tests to ensure that they have been properly classified. Testing to characterize the degradation of tetraphenylborate solids is also under way, but results are not yet available.

Benzene Retention and Release—Several tests have been performed in an effort to determine visually where benzene is retained in tetraphenylborate slurries. In these tests, benzene was tinted using a red dye and then added to a tetraphenylborate slurry. It was found through these tests that when benzene is first added, it adsorbs onto the tetraphenylborate solids. As larger amounts of benzene accumulate in the slurry, "suspended benzene" is observed, trapped between agglomerated tetraphenylborate particles. The suspended benzene was observed to evaporate quickly upon contact with air. SRTC suspects that this suspended benzene is the source of the "readily releasable benzene" released to the vapor space in Tank 48 when the mixer pumps are operated after a quiescent period.

Further benzene retention and release testing is under way, including large-scale demonstrations using 6-foot-tall columns with in-situ benzene generation and a floating solid layer similar to that in Tank 48. The columns have sample ports that allow benzene to be detected over a range of heights. To date, benzene has been detected exclusively in the floating solids layer. Smaller-scale tests will explore the effects of single parameters such as temperature, weight percent solids, and sodium concentration on benzene retention and release.

ITP Tank Cooling Systems. The ITP chemistry program has found that tetraphenylborate decomposition rates increase dramatically with increasing temperature. Accordingly, temperature controls are an important component of the safety strategy for future ITP operations. However, cooling-water systems have suffered outages in the past, so their reliability for future ITP operations is questionable. Although tank temperatures can be regulated to some degree by controlling heat inputs, such as the duration and speed of mixer pump operations, it is not yet clear how WSRC intends to control temperatures in Tanks 48 and 49 once full-scale ITP operations begin. The Board staff will evaluate how WSRC plans to implement reliable temperature controls for ITP.

5. Future Staff Actions

The Board staff will continue to review the implementation of Recommendation 96-1 at SRS, particularly with regard to ITP's safety systems, resolution of the vapor mixing issue, and the ITP chemistry program.