97-0001383

DEFENSE NUCLEAR FACILITIES SAFETY BOARD

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April 11, 1997

Mr. Mark B. Whitaker, Jr.
Department of Energy
1000 Independence Avenue, SW
Washington, DC 20585-1000

Dear Mr. Whitaker:

Enclosed for your information and distribution are 25 Defense Nuclear Facilities Safety Board staff trip reports.

Sincerely,

Andrew L. Thibadeau
Information Officer

Enclosures (25)

DEFENSE NUCLEAR FACILITIES SAFETY BOARD

January 29, 1996

MEMORANDUM FOR: G. W. Cunningham, Technical Director

COPIES: Board Members

FROM: R. N. Robinson

SUBJECT: Report on Status of Combined Lower Flammability Limit Issue for Tank 48 at In-Tank Precipitation, Savannah River Site

1. **Purpose:** This report documents a Defense Nuclear Facilities Safety Board's (Board) staff review of the high benzene releases in Tank 48 at the In-Tank Precipitation (ITP) facility resulting in a potential inadequacy in the ITP safety analysis. This review was conducted by D. Lowe, J. Roarty, R. Zavadoski, and R. Robinson on January 22-23, 1996.

2. **Summary:** Recent pump mixing operations in ITP Tank 48 have resulted in benzene release rates exceeding Authorization Basis (AB) limits. During ITP Tank 48 Radioactive Operations Commissioning Test Program (ROCTP) tests conducted on December 1, 1995, slurry pumps were shut down when higher than expected benzene releases occurred during slurry pump operation. Further analysis indicated that the releases exceeded the rates specified in the AB. A potential inadequacy in the ITP safety analysis was declared and led to a positive unresolved safety question (USQ). The slurry pumps were restarted on December 8, 1995, after approval of a Justification for Continued Operation (JCO), allowing single pump operation with controls in place to insure that the benzene releases were maintained within the ITP AB. On January 3, 1996, analysis determined that post-slurry pump operation release rates exceeded the ITP AB and slurry pump operation was suspended again. Westinghouse Savannah River Company (WSRC) is proposing a second, short-term JCO to remove the excess benzene from Tank 48 and assure safety by inerting the vapor space instead of limiting the fuel concentration in the vapor space as required in the current AB. This second JCO will permit operation with an alternate safety basis for approximately three weeks.

   These unexpected events indicate a lack of basic understanding of the mechanisms for benzene generation and release of tetraphenylborate (TPB) in the Tank 48 environment. The Board's staff agrees with the Department of Energy (DOE) that the large amount of benzene present in Tank 48 must be removed in the near term. The staff also believes that further additions of waste or sodium tetraphenylborate (NaTPB) should be suspended until the generation and release mechanisms are better understood, safety measures are in place, and changes have been made to the ITP AB.

3. **Background:** An important assumption in the current Safety Analysis Report (SAR) Addendum I for ITP, WSRC-SA-15, Rev. 8, is that Tank 48 be operated in such a manner that, on loss of ventilation, no more than three days could elapse before the Composite

4. Discussion/Observations: Several technical issues were discussed during the review.

a. Benzene Generation: Laboratory tests have been performed and confirmed the magnitude of the generation of benzene by radiolytic, thermal, and catalytic decomposition of the NaTPB. Studies of radiolysis of TPB now confirm that there is no "trapped benzene" released by washing in Tank 48. However, at an assumed G-value of 1.0, radiolytic decomposition can only account for one percent of the benzene presently being generated in Tank 48. Thermal decomposition of NaTPB is well understood, and it can only account for one percent of the benzene being generated in Tank 48 based on bulk, not localized, tank temperatures. Copper, a known catalyst for the decomposition of TPB, has been measured at 1.7 ppm in Tank 48. The catalytic effect observed in Tank 48, as well as in the laboratory, begins with a four to seven week incubation period, when little or no decomposition occurs, followed by an increasing rate of decomposition. The incubation period may be caused by the slow depletion of some inhibiting species or the slow generation of some intermediate required for the catalysis reaction. The catalytic effect of copper accounts for approximately 10 percent of the benzene being generated in Tank 48. The incubation period observed in Tank 48 is consistent with copper catalysis tests in the laboratory. Since the bulk of the decomposition of NaTPB appears to be catalytic in nature, an investigation of catalytic effects is being revisited in an attempt to understand the mechanism of the decomposition observed in Tank 48. The effect of temperature on copper catalysis is known and is significant (a thousand-fold rate increase for a forty degree temperature change). There is a lesser effect of concentration on catalytic decomposition (i.e., decomposition is directly proportional to copper concentration). It is conceivable that local high temperatures or "hot spots" are causing local benzene generation.

Over 3,500 kg of benzene have been generated in Tank 48 since ROCTP testing was started; however, over 2,400 kg remain in the aqueous phase as free benzene. The excess TPB has been decomposed and law of mass action on the equilibrium of the TPB species has caused some of the radioactive cesium to pass to the solution from the precipitate.

The net result is that the benzene generation mechanism is not well understood. Unless the mechanism for benzene generation is understood, the safety of the facility cannot be assured.

b. Benzene Release: Benzene releases (but not generation) in Tank 48 have been attributed to pump operation. There is evidence that any disturbance of the solution in the tank releases benzene. Since the free benzene in Tank 48 is well above its solubility in the aqueous phase, a second liquid phase of benzene should form. However, no significant separate phase has been observed on the tank liquid surface. Some early laboratory observations indicate that the free benzene could adsorb onto the surface of the TPB precipitate that could easily be desorbed by agitation. Presently, the rate of release is controlled by pump operation. Benzene is released when the pump is turned on and stops releasing when it is turned off. However, it is conceivable that some other energy source (e.g., mechanical, electrical, or chemical) could also cause benzene to desorb from the TPB surface quickly and would form an organic layer on the liquid surface. Because of evaporation, the fuel concentration in the vapor phase would rise quickly by an order of magnitude to levels higher than seen before. These mechanisms would not be controlled by pump operation and would be a serious threat to the safety of the ITP process. Benzene release is only understood empirically. Unless the mechanism of benzene release is understood, the safety of the facility cannot be assured.

c. Inerting: For flammability purposes, the vapor space in Tank 48 contains three components: fuel (benzene and a small amount of hydrogen from radiolysis), oxidant (oxygen from in-leakage of air), and inert (nitrogen purposely injected and nitrogen from in-leakage of air). Common industrial practice for flammability control is to control either the fuel or oxidant and ignition sources. The current SAR for ITP specifies fuel level flammability control. If the fuel is kept to less than 13,700 ppm (the CLFL), there is no mixture of oxidant-inert that can make the mixture flammable. This method is called fuel control. Using fuel control, the Limiting Condition of Operation (LCO) limit is 25 percent of the CLFL or 3,425 ppm fuel.

Higher fuel levels can still be nonflammable if the oxidant (oxygen in this case) can be controlled. The safety basis worst case fuel composition is 9:1 benzene to hydrogen (from radiolysis). At this fuel composition, the Minimum Oxygen for Combustion (MOC) is calculated at nine percent (i.e., there is no fuel inert mixture that is flammable if oxygen is kept below nine percent). Tank 48 tests indicate that the fuel composition is closer to 99:1, raising the MOC to above 10 percent. WSRC is proposing inerting (oxidant control) as the long-term flammability control method. The LCO limit proposed is 6.9 percent oxygen (well below the MOC) to allow for a margin of safety and accounting for instrument uncertainties. Oxidant control relies on relatively airtight vessels or slight positive pressures to minimize in-leakage. If air is the source of the oxidant, in-leakage of oxygen is always a mixture of 4:1 inert-to-oxygen. With inerting as the basis for maintaining flammability safety, the process would be to "button up" the tank on loss of ventilation (supply and/or exhaust). The button-up process includes termination of exhaust fan operation, closure of stack exhaust dampers, termination of pump operation, termination of liquid additions, establishing a small nitrogen purge to the tank within eight hours, closure of the conservation vent bypass valve when there is no nitrogen flow, isolation of nonessential nitrogen loads, and control of Tank 48 breeches. The potential exists for problems to arise when Tank 48 is in the button-up state and includes stratification of benzene in the vapor space, additional oxidant introduction other than in-leakage (e.g., radiolysis), loss of effectiveness of the tangential directed purge flow at reduced flow conditions, and tank pressurization causing benzene and contamination leakage out of the tank.

d. Short-Term Plan: WSRC is preparing the second JCO to allow single and multiple pump operation with tank inerting and a limit of 25 percent of CLFL during slurry pump operation as the safety basis. WSRC is also installing a backup nitrogen purge system to improve the overall reliability of inerting. Procedures are being prepared and operator training is continuing in preparation for operating under the second JCO.

e. Long-Term Plan: The Savannah River Technology Center (SRTC) will be conducting experiments to understand the mechanisms for benzene generation and release in Tank 48. Tests will include catalytic effects on decomposition of TPB, effect of agitation on benzene release, mass transfer rates of benzene release, and radiolysis. WSRC plans to develop a revised AB based on inerting as the method to control flammability. This will require that existing systems be upgraded to safety class or that new safety class systems be installed. The draft WSRC schedule shows continued operation of ITP in the April 1996 time frame. Necessary upgrades may not be complete by then so further delays can be expected.