DEFENSE NUCLEAR FACILITIES SAFETY BOARD

April 26, 1995

MEMORANDUM FOR: G. W. Cunningham, Technical Director

COPIES: Board Members

FROM: Richard E. Tontodonato, Technical Staff

SUBJECT: Trip Report - Review of Hanford Site High-Level Waste Tank Safety and Characterization, March 14-16, 1995

1. **Purpose:** This trip report documents a visit by Board staff members (David Lowe, Randall Robinson, and Richard Tontodonato) to the Hanford Site on March 14-16, 1995, to review Westinghouse Hanford Company (WHC) efforts to develop a new approach for safety-related characterization of Hanford's high-level waste tanks.

2. **Summary:** WHC is continuing to develop a new approach for safety-related characterization of Hanford's high-level waste tanks that would significantly reduce sampling requirements. The new strategy would declare a tank safe, based on the characteristics of the waste surface and the absence of flammable or toxic vapors in the tank dome space. The principal difficulty with this approach is that it requires deducing and analyzing all possible hazardous conditions in tanks which have not been characterized. Significant portions of the new strategy are based on simplified models and simulants that may not adequately represent tank wastes, and WHC has not determined how or when postulated waste properties will be verified with actual tank waste samples.

3. **Background:** Characterizing the tank wastes is key to resolving high-level waste tank safety issues at the Hanford Site. On July 19, 1993, the Board issued Recommendation 93-5, which addresses the need for the Department of Energy (DOE) to undertake a comprehensive reexamination and restructuring of the characterization effort. The recommendation sets goals of two years for completing safety-related sampling and analysis for watch list tanks and three years for other tanks. The Board accepted DOE's Implementation Plan on March 25, 1994, and members of the Board staff have visited the Hanford Site seven times since November 1993 to review implementation of Recommendation 93-5. This review was conducted as a follow-up to the previous reviews and in preparation for a public hearing held in Richland, Washington, on March 29, 1995.

4. Discussion:

a. High-level waste tank safety strategy: In the original Data Quality Objectives (DQO) documents prepared in accordance with the DOE Recommendation 93-5 Implementation Plan, WHC proposed to determine whether the high-level waste tanks were safe by sampling and analyzing full-depth core samples from each tank. Based on difficulties subsequently encountered in obtaining core samples and on a desire to minimize tank sampling, WHC is now developing a justification for only obtaining surface and vapor samples from most tanks.

This approach requires that WHC deduce all possible hazardous conditions which could have developed in the tanks over the past fifty years and assess whether or not vapor and surface sampling can adequately detect them. This difficult task is further complicated by the limited information available regarding the exact nature of the tank wastes. Sampling to date has been limited, and historical records are typically not complete, reliable, or necessarily representative due to inadequate operational controls in the past as well as chemical and radiolytic processes occurring in the tanks. Because of these problems, WHC has relied extensively on simplified models and simulants to develop the new strategy. Key elements of the strategy and their shortcomings are summarized below:

1. Accident initiators: WHC's surface sampling strategy assumes that accidents can only be initiated by events in the tank dome space or on the waste surface. This requires defining the depth beneath the surface which can be affected by a surface initiator as well as analyzing the potential for subsurface initiators.

   A consultant to WHC presented a simplistic analysis of how a surface event (e.g., a hot object falling onto the waste) can affect material below the waste surface. The event was modelled as purely conductive heat transfer between two infinite planes at different temperatures. The analysis concluded that only the top four inches of waste are likely to be affected by surface events. Although WHC agreed with this conclusion, this analysis is flawed. A review by the Board staff found that the consultant did not analyze the chosen model correctly, underestimating the affected depth by more than a factor of two. Further, the model assumes the waste surface is a uniform, impenetrable solid. Convective heat transfer is neglected, as are cracks and holes in the surface and the likelihood that an impacting object will penetrate some depth into the waste.

   If the waste below the surface is dry and reactive, a subsurface initiator such as a local hot spot, criticality excursion, electrical short, or lightning strike on an instrument tree or other equipment in the waste could set off a runaway chemical reaction. WHC has analyzed the potential for hot spot formation in ferrocyanide sludges and concluded it is unlikely, but the likelihood of forming hot spots in other waste types has not been assessed. WHC has also evaluated the initiation potential for equipment in the tanks, criticality, and lightning, and concluded that lightning was the only credible subsurface initiator that was not already mitigated. WHC has not yet decided what must be done to ensure lightning will not cause tank accidents, and it is not clear when a course of action will be defined. As stated in the report of the February 28 - March 2, 1995, staff review of tank farm electrical systems, this problem warrants prompt attention.

2. Fuel-nitrate reactions: The proposed strategy will not attempt to determine which tanks contain reactive mixtures of fuels and oxidizers, such as non-volatile organic materials and/or ferrocyanide compounds mixed with nitrates. Instead, WHC intends to assess whether the waste surface is wet enough to preclude propagating exothermic reactions. This approach requires understanding how water is distributed in the tanks and how much water is required to prevent reactions from propagating.

WHC believes that saltcake wastes may become dry and plans to assess whether saltcakes contain enough fuel to present a hazard. However, WHC believes that sludges, with few exceptions, are uniformly wet and will remain wet for the foreseeable future. These conclusions are based on studies of moisture retention in kaolin clay, limited work with ferrocyanide sludge simulants, the limited sampling results currently available, and modelling of evaporation processes in tanks. WHC believes that most sludges contain small (micron range) particles, resulting in capillary forces that are strong enough to preclude global water loss and prevent dryout of locally heated regions. However, WHC acknowledges that shallow tanks and tanks with higher decay heat loads may still become dry. In fact, low moisture contents have been found in several sludge samples (1 to 17% in tank 241-BX-101, 3 to 9% in tank 241-BX-108, as low as 13.5% in tank 241-C-103). The staff believes that WHC's conclusion that sludges are uniformly wet needs to be verified by a core sampling program that explores the relevant variables (e.g., sludge type, decay heat load, waste height, interim stabilization, etc.) in actual waste tanks. WHC agrees that actual wastes need to be more thoroughly investigated, but has not yet decided how to do this.

WHC is also testing waste simulants to define the energy content of ferrocyanide compounds and various organic constituents in wastes. This testing defines the fuel concentration required to sustain a propagating exothermic reaction in dry materials and the amount of water needed to prevent such reactions. A WHC consultant has developed a thermodynamic model showing that the energy content required to sustain a propagating reaction is directly proportional to the ignition temperature of the material. Based on this model, WHC has concluded that wastes with an energy content below 290 calories per gram or containing greater than 20 weight percent moisture cannot sustain a propagating reaction. Experimental results for several simulant materials support both criteria.

However, testing with actual wastes has been limited to specimens too small for propagation tests, and it has not been proven that the simulants accurately represent the propagation behavior of real wastes. Furthermore, the staff believes that WHC has not adequately shown that its propagation model will be conservative when applied to real wastes. The principal staff concerns are summarized in the appendix to this report.

3. Other organic reactions: Organic liquids in the tanks have the potential to undergo pool fires or, if entrained in saltcake or sludge, wick-stabilized fires. WHC believes liquid organics can be detected by vapor sampling. While significant organic pools will likely emit detectable vapors, WHC has not defined the screening criteria for organic vapors. Also, it has not been demonstrated that vapor sampling will reliably detect organic liquids entrained in sludge or saltcake.

4. Flammable gases: WHC plans to continue screening for flammable gases using vapor sampling at a single location in each tank. This appears to be adequate for assessing the steady-state flammable gas concentration. Continuous hydrogen monitoring instruments have been installed in all tanks suspected of undergoing periodic gas releases based on observed level fluctuations.

b. Tank characterization technical basis: WHC stated that the DQO for safety-related tank waste characterization will be completed by April 1995, and the DQOs for waste retrieval and disposal will be completed by June 1995. Overall integration of the sampling program is scheduled for August 1995.

c. Tank sampling status: WHC is still far behind the sampling milestones DOE committed to in the Recommendation 93-5 Implementation Plan. As of March 13, 1995, the following sampling has been accomplished:

- Rotary mode core sampling - 1 tank, variable recovery
- Push mode core sampling - 2 tanks good recovery, 2 tanks poor recovery
- Auger sampling - 10 tanks, variable recovery
- Liquid grab sampling - 21 tanks
- Vapor sampling - 26 tanks

WHC personnel believe they now understand which types of waste are suitable for push mode sampling and expect to achieve more consistent results in future push mode attempts. WHC has restricted the rotary mode sampler to push mode operations due to poor sample recovery in segments requiring rotary drilling. WHC has consulted with the Army Corps of Engineers and also assembled a Tank Sampling Advisory Panel to provide recommendations on improving the existing core and auger samplers and developing new tools. WHC is currently evaluating a list of 40 suggestions from these reviewers. WHC has also assessed ways to improve the availability of the rotary mode system and is evaluating 47 potential improvements. By June 1995, WHC plans to field test improvements to the rotary mode system on an actual tank.

d. Laboratory issues: Because of the slower than expected pace of tank sampling, WHC no longer plans to use the PNL 325 laboratory or the Idaho National Engineering Laboratory (INEL) for routine tank waste sample analyses. WHC does not expect to use INEL in the future, and expects to use the PNL 325 laboratory for research and development work and for unique analyses not available at the WHC 222-S laboratory. The associated reduction in the PNL 325 workforce, coupled with the difficulty of locating and hiring qualified radiochemists, could make it difficult for the analytical laboratories to keep up with sampling operations if WHC succeeds in significantly improving the sampling rate.

5. **Future Staff Actions:** The staff will continue to closely follow implementation of Recommendation 93-5. The staff plans to conduct a video conference with WHC and DOE in late April or early May 1995 to further discuss proposed revisions to the characterization program strategy and efforts to improve sampling techniques.

APPENDIX

Staff Concerns with Proposed Westinghouse Hanford Company Moisture and Energetics Limits

The new limits Westinghouse Hanford Company (WHC) has proposed to identify wastes which may undergo runaway chemical reactions are based entirely on testing of simulant materials with much simpler compositions than actual wastes. Testing with actual wastes has been limited to specimens too small for propagation tests, and it has not been proven that the simulants accurately represent the propagation behavior of real wastes. Furthermore, the Defense Nuclear Facilities Safety Board (Board) staff believes that WHC has not adequately shown that its propagation model will be conservative when applied to real wastes. The principal Board staff concerns are summarized below:

- The 290 calories per gram energetics criterion was obtained using data for sodium acetate, which has the highest ignition temperature of any simulant tested. Using the ignition temperature for <u>any</u> of the other simulant materials (e.g., ferrocyanide or hydroxyethylethylenediaminetriacetate (HEDTA)) would result in a considerably lower safety limit. WHC's consultant used the ignition temperature for sodium acetate because he believed it provided a "reasonable (not too conservative)" energy limit. While this limit is conservative relative to the simulant test data, it has not been shown that it will be conservative relative to actual waste behavior.

- Propagation testing used nominally dry reagents, but the actual starting moisture content of organic simulants was not determined. Water absorbed or adsorbed onto the starting materials will inhibit propagating reactions. This will result in overestimating the energy needed to start a reaction in dry material and underestimating the amount of water needed to prevent a reaction. (Moisture measurements for tank waste samples are done using thermogravimetric analysis, which will detect all absorbed water and some of the adsorbed water.)

- WHC has not estimated the significance of other errors built into the model. The model assumes the starting temperature of the wastes is negligible (i.e., 0°C), whereas the actual wastes have temperatures up to 94°C (tank 241-SX-108). The model also assumes that the heat capacities of the reactants and the combustion products are equal, and used average (not worst case) simulant heat capacities instead of actual waste properties. Similarly, the magnitude and effect of errors in measuring ignition temperatures and other test parameters have not been considered.