July 20, 2001

The Honorable Jessie Hill Roberson
Assistant Secretary for
Environmental Management
Department of Energy
1000 Independence Avenue, SW
Washington, DC 20585-0113

Dear Ms. Roberson:

The Defense Nuclear Facilities Safety Board (Board) has been evaluating preparations at the Savannah River Site (SRS) to start up the HB-Line neptunium/plutonium oxide process, known as HB-Line Phase II. Safe and successful operation of HB-Line Phase II is an important step toward stabilizing actinide solutions at SRS, as committed to by the Secretary of Energy in the Department of Energy's Implementation Plan for the Board's Recommendation 94-1, *Improved Schedule for Remediation in the Defense Nuclear Facilities Complex*. The Board believes thorough and timely analysis of hazards and identification of controls are essential to the success of this project and to the avoidance of further delays in stabilizing these hazardous materials.

The Board's staff has identified several potential safety issues associated with this activity. Some of these issues appear to be the result of insufficient hazard analysis. In general, the hazard identification process used for this project does not appear to be as comprehensive as the Process Hazard Analysis methodology recommended in DOE-STD-3009-94, *Preparation Guide for U.S. Department of Energy Nonreactor Nuclear Facility Safety Analysis Reports.* The limitations of the methodology used at HB-Line Phase II may have contributed to some accident scenarios not being evaluated effectively in the contractor's hazard analysis.

The Board is aware that additional hazard analysis is being performed, and anticipates receipt of the findings of this analysis, as well as the identification and implementation of additional controls that may be warranted. The Board was pleased to see that a safety system failure mode evaluation has been performed to identify potentially unsafe failure modes for some existing HB-Line systems that provide active safety controls. A similar evaluation may be appropriate for other HB-Line safety systems, including those that perform alarm functions.

During a recent visit to SRS, the Board was briefed on HB-Line Phase II startup preparations. The Board is aware that there are continuing discussions between the Board's staff and SRS personnel, and that work to address staff questions and issues is ongoing.

The enclosed reports prepared by the Board's staff identify several issues that warrant further consideration by project personnel.

Sincerely,

John T. Conway
Chairman

c: Mr. Greg Rudy
Mr. Mark B. Whitaker, Jr.

Enclosures

DEFENSE NUCLEAR FACILITIES SAFETY BOARD

Staff Issue Report

June 25, 2001

MEMORANDUM FOR: J. K. Fortenberry, Technical Director

COPIES: Board Members

FROM: R. Robinson, M. Duncan

SUBJECT: Chemical Process Safety, HB-Line Phase II

This report documents issues identified by the staff of the Defense Nuclear Facilities Safety Board (Board) during a review of the chemical processes described in the authorization basis for the HB-Line Phase II startup.

Overview. HB-Line Phase II operations are scheduled to commence in December 2001. The operations involve converting 34,000 liters of H-Canyon plutonium nitrate solutions to oxide powder. The process steps include valence adjustment, separation through ion exchange, concentration, oxalate precipitation, filtration, and calcination to oxide.

Process Chemistry Issues. After performing a review of the authorization basis for HB-Line Phase II, the staff identified weaknesses in the analysis of two hazards: ion exchange resin explosions and chemical reactions in process tanks.

Resin Explosions—Since 1962, there have been no fewer than nine documented incidents of fire, explosion, and/or vessel rupture in anion exchange vessels. These incidents, categorized as "resin explosions," have occurred under various conditions of temperature and nitric acid concentration. All of the systems involved were exchanging either plutonium, neptunium, curium, or uranium.

A document commissioned by the Savannah River Site (SRS) contractor, *Task 15-Phase I Assessment of Additional Pressure Relief Capability 221 HB-Line Anion Exchange Columns,* identified several conditions contributing to a possible resin explosion:

- exposure of resin to greater than 9 molar nitric acid
- exposure of resin to high temperature
- allowing resin to dry

- exposure of resin to strong oxidants other than nitric acid, such as permanganate or chromate ions

- exposure of resin to high radiation doses

- allowing resin to remain in a stagnant, nonflow condition while loaded with exchanged metal and/or in contact with process concentrations of nitric acid

- exposure of resin to strong reducing agents, such as hydrazine

- exposure of resin to catalytic metals such as iron, copper, or chromium

The process design and authorization basis for HB-Line Phase II address some, but not all, of these conditions. Sufficient passive and active controls are designed into the HB-Line Phase II process to prevent possible high nitric acid concentrations or resin dryout. The effect of temperature on the resin exotherms was carefully documented in the March 10, 2000, Savannah River Technology Center (SRTC) report *Qualification of Reillex™ HPQ Anion Exchange Resin for Use in SRS Processes*. The authorization basis specifies controls for temperature effects based on this document. These studies also indicate that the maximum expected radiation dose to the resin during 1 year is much lower than would be required to pose a safety concern. Finally, the design of the process prevents the use of oxidants other than nitric acid, such as permanganate or chromate ions, in the resin columns. However, several conditions that could lead to a resin explosion were not adequately addressed in the hazard analysis, including a stagnant resin bed, exposure to catalytic metal ions, and the possible introduction of strong reducing agents to the resin. It would be appropriate for these three conditions to be identified and analyzed, and for associated controls important to safety to be incorporated, if warranted, in the authorization basis and operating procedures.

Chemical Addition—The combination of certain chemicals during the HB-Line Phase II process will produce heat from exothermic reactions. Some reactions can also generate substantial volumes of gas. A high rate of chemical addition can easily cause an eructation in addition to a large evolution of heat. In a closed process vessel, a sudden generation of heat and gas could result in an explosion caused by overpressure. An informal analysis performed by the SRS contractor determined that the presence of the "ever open" vessel vent system and the relatively low heats of reaction for the potential chemical combinations eliminate this safety issue. Discussions between the staff and the contractor led to agreement that reactions caused by chemical additions to the process tanks are not likely to cause an accident resulting in serious injury to a worker. However, this scenario was not included in the development of the authorization basis and its supporting documents.

The staff believes the hazard analysis for HB-Line Phase II was not consistent with chemical processing industry practice whereby potential runaway reactions in each process vessel are analyzed. However, by installing orifices to limit addition rates and limiting the size of portable chemical addition vessels, efforts are being made to provide controls for hazards originally missed.

A formal analysis of chemical additions to the HB-Line Phase II process has recently been completed, and a determination of the maximum safe addition rates is expected in mid-July 2001. On the basis of preliminary results from the formal analysis, the contractor believes its previous conclusions are valid.

Conclusion. The Board's staff concludes that the contractor has not throughly analyzed and formally documented preventive measures for all the known causes of resin explosion, nor has the analysis of chemical eructations as yet been completed and formalized. A formally documented analysis is needed to support the implementation of adequate controls for HB-Line Phase II.