July 31, 2002

Dr. Raymond Cooperstein
10935 Deborah Drive
Potomac, Maryland 20854

Dear Dr. Cooperstein:

The Defense Nuclear Facilities Safety Board (Board) has received your letter of June 24, 2002, regarding stabilization and packaging activities being pursued by the Department of Energy (DOE). The Board has encouraged DOE to place its hazardous materials in a stable form and in robust packaging in a timely manner as set forth in Recommendation 94-1, *Improved Schedule for Remediation in the Defense Nuclear Facilities Complex*.

The Board has reviewed and agreed with each revision of DOE-STD-3013, *Stabilization, Packaging, and Storage of Plutonium-Bearing Materials*, and will also review any subsequent revisions to the standard. The Board believes that plutonium-bearing materials packaged in accordance with this standard can be safely stored for an extended period of time, and continues to endorse use of this standard throughout the DOE complex. As noted in the enclosed correspondence from the Board to DOE, the Board continues to review implementation of the standard at sites that are packaging their plutonium inventories, and to press DOE to resolve issues associated with the standard and its implementation.

The Board appreciates your continued interest and insights regarding this important effort.

Sincerely,

John T. Conway
Chairman

c: Mr. Mark B. Whitaker, Jr.

Enclosures

Enclosure 1

May 3, 2001

The Honorable Carolyn L. Huntoon
Acting Assistant Secretary for
Environmental Management
Department of Energy
1000 Independence Avenue, SW
Washington, DC 20585-0113

Dear Dr. Huntoon:

In response to the Defense Nuclear Facilities Safety Board's (Board) Recommendation 94-1, *Improved Schedule for Remediation in the Defense Nuclear Facilities Complex*, the Department of Energy (DOE) is stabilizing and repackaging nonprogrammatic plutonium metal and oxide in accordance with DOE-STD-3013, *Stabilization, Packaging, and Storage of Plutonium-Bearing Materials*. To prevent overpressurization of containers during long-term storage, the standard requires limiting the moisture content of plutonium oxide materials to a very low level. The standard requires that the moisture content of each container of plutonium oxide be determined using loss-on-ignition measurements, but allows alternative methods when approved by DOE. Based on testing of certain plutonium forms at Los Alamos National Laboratory (LANL), the Office of Environmental Management, in a letter dated May 19, 2000, authorized use of the supercritical fluid extraction (SFE) process as an alternative means of measuring the moisture content of all oxide materials being packaged to DOE-STD-3013 for long-term storage.

The Board was recently informed of test results from moisture measurements using SFE at Hanford. These results indicate that the moisture content in plutonium oxides precipitated from solution using magnesium hydroxide is underestimated. The testing performed by LANL may not have been sufficiently representative to identify this problem with SFE being experienced by Hanford. The Board believes the authorization to use SFE is too broad, and needs to be temporarily rescinded pending DOE's further evaluation of the suitability of SFE for these measurements.

The Board notes that Hanford's moisture measurements using the approved loss-on-ignition method are also underreporting the moisture content for this hygroscopic material. This error appears to result from what may be a more fundamental problem. DOE-STD-3013 does not specifically control ambient glovebox conditions following stabilization of material. The humid glovebox environment at Hanford can allow plutonium oxide materials to quickly regain a significant amount of moisture following stabilization. For the loss-on-ignition method of moisture measurement, a humid glovebox environment could also contribute to moisture measurement errors, as observed at Hanford.

The Board requests to be briefed on the actions planned by DOE to resolve issues associated with the lack of requirements in the standard for glovebox ambient conditions and the use of SFE for moisture measurements. This briefing should include the results of any evaluations that have been performed to resolve these issues.

Sincerely,

John T. Conway
Chairman

c: Mr. Mark B. Whitaker, Jr.

Enclosure 2

July 12, 2002

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

Dear Ms. Roberson:

The staff of the Defense Nuclear Facilities Safety Board (Board) recently reviewed changes to approved guidance for verifying thermal stabilization of plutonium oxide in Department of Energy (DOE) Standard 3013-2000, *Stabilization, Packaging, and Storage of Plutonium-Bearing Materials*. The intent of the verification is to confirm that impurities with the potential to cause pressurization during long-term storage have been removed through proper stabilization at 950°C.

The Board believes that thermogravimetric analysis (TGA) coupled with either a mass spectrometer (TGA-MS) or a Fourier transform infrared detector (TGA-FTIR) can be an appropriate method for accomplishing this verification. However, the approval memorandum of May 14, 2002, only provides guidance for identifying the presence of water, and excludes other impurities with the potential to generate pressure. Additionally, although the approval encompassed all plutonium oxide materials, the referenced technical basis identifies the need for further research before these methods can be applied to impure oxide materials.

The Board notes that the Rocky Flats Environmental Technology Site (RFETS) has developed an approach that may address these concerns and appears to be implementing TGA-FTIR in an appropriate manner. With some modifications, the procedures developed at RFETS may serve as a model for other sites.

The enclosed report prepared by the Board's staff provides additional detail related to these concerns. Pursuant to 42 U.S.C. § 2286b(d), the Board requests a report within 60 days of receipt of this letter that addresses the issues outlined in the enclosed staff report.

Sincerely,

John T. Conway
Chairman

c: Ms. Barbara A. Mazurowski
Mr. Mark B. Whitaker, Jr.

Enclosure

DEFENSE NUCLEAR FACILITIES SAFETY BOARD

Staff Issue Report

June 20, 2002

MEMORANDUM FOR: J. K. Fortenberry, Technical Director

COPIES: Board Members

FROM: J. Plaue

SUBJECT: Verification of Plutonium Oxide Stabilization

This report documents a review performed by the staff of the Defense Nuclear Facilities Safety Board (Board) of approved guidance for verifying thermal stabilization of plutonium oxide as defined in accordance with Department of Energy (DOE) Standard 3013-2000, *Stabilization, Packaging, and Storage of Plutonium-Bearing Materials*. Findings from a review of the relevant documentation and a June 6, 2002, visit to the Rocky Flats Environmental Technology Site (RFETS) by staff members R. Kasdorf and J. Plaue are summarized below.

Background. DOE Standard 3013-2000 requires the verification of thermal stabilization for each batch of plutonium oxide stabilized. The standard specifies the use of a loss-on-ignition (LOI) test to verify that impurities with the potential to cause pressurization have been removed. However, passing the LOI criteria may be difficult for impure oxides because of the high volatization of chloride and fluoride compounds. While such impurities contribute to the loss of mass during LOI, they are generally acceptable from a long-term storage standpoint. To address this issue, DOE's Assistant Secretary for Environmental Management issued a memorandum on May 14, 2002, approving the use of thermogravimetric analysis (TGA) coupled with either a mass spectrometer (TGA-MS) or a Fourier transform infrared detector (TGA-FTIR) as alternative test methods. TGA measures loss of mass as a function of temperature. The coupling of the additional analytical instruments allows for a semi-quantitative assessment of which chemical species (e.g., water, carbon dioxide, organics) are volatilizing as the temperature increases.

Department of Energy Direction. The staff has reviewed DOE's approval memorandum and its attached guidance, as well as the referenced technical basis found in a Los Alamos National Laboratory report, *Certification of Thermal Gravimetric Analysis with Moisture Detection Systems for Water Determinations on 3013 Materials*
(LA-UR-02-2233). The staff identified the following issues:

a: DOE's approval memorandum gives general approval for the use of TGA-FTIR/MS methods with the caveat that each site must provide documentation of an adequate technical

basis for the material types to be analyzed. However, the findings in LA-UR-02-2233 refer to work performed exclusively on surrogate or pure oxide materials. Studies using more representative matrices have not yet been completed. The referenced technical basis clearly states, "The application of TGA-FTIR/MS techniques to impure materials is underway as stated in the experimental section. An evaluation of those data is needed before an unqualified endorsement of this method is made."

a: In general, the DOE guidance addresses exclusively the detection of moisture. While moisture is the primary concern in a fully stabilized material, other potentially problematic impurities indicative of incomplete stabilization (e.g., organics, carbonates, and sulfates) could be missed unless mass loss from sources other than moisture is carefully considered. The guidance attached to the DOE approval memorandum specifies that mass numbers 17 and 18 (corresponding to water and the hydroxyl ion) are of interest for TGA-MS. The document provides no guidance for TGA-FTIR, except that the sites are allowed to choose their own regions of interest on the infrared spectrum, provided they document possible interferences. Both analytical techniques have the capability to detect and differentiate among various volatile species and could be used to identify inadequately stabilized materials if properly applied. More definitive guidance from DOE is warranted.

a: The DOE guidance allows heat-up rates of up to 20°C/minute. However, the data presented in the technical justification for TGA-FTIR/MS does not appear to justify the use of rates of temperature increase up to 20°C/min. In addition, no guidance is given for gas flow rate. The supporting data show significant differences in the integrated peaks when heat-up or flow rates are varied. It is unclear whether these differences could have a significant impact on the accuracy of the measurements.

Implementation at Rocky Flats Environmental Technology Site. The staff recently reviewed the proposed use of the TGA-FTIR technique at RFETS. As allowed by the DOE guidance, the contractor (Kaiser-Hill) has chosen the minimum specified sample size (2 mL) and the maximum heat-up rate (20°C/min). The anticipated throughput of the two TGA units coupled to one FTIR is approximately one sample analysis per hour.

Analysis Technique—During each analysis, the infrared (IR) spectrum from 1000 to 4000 cm^{-1} will be captured as a function of time. Additionally, the contractor is considering retaining the TGA-FTIR data as part of the information package for each container. For the analysis of moisture, the contractor will monitor three regions of the IR spectrum (1480–1590, 1590–1700, and 3850–4000 cm^{-1}). This approach should minimize the potential for interference from other constituents.

The contractor is currently developing the procedure for data analysis and the acceptance criteria. As explained to the staff, the procedure will generally involve the qualitative comparison of

mass loss peaks produced through TGA with moisture-related peaks detected by FTIR as a function of time. The basic philosophy behind this approach is to confirm that mass losses are in fact due to moisture. In the event that mass losses do not correlate with FTIR indications of water, the contractor will rely on the judgment of subject matter experts to determine the source of the losses based on the mass-loss profile and IR data. However, the interpretation of IR spectra is not entirely precise and involves the comparison of countless spectra contained in reference books. The staff was informed that commercially available spectral matching software would be ineffective at analyzing gas-phase inorganic species that may be present.

Staff Observations—The RFETS contractor's proposed approach to the use of TGA-FTIR analysis appears to be appropriate. However, the staff made the following observations that also apply generically to the newly approved DOE guidance:

a: The current equipment setup may prohibit the detection of some inorganic vapor species due to condensation in sample lines. The gas transfer lines between the TGA and FTIR units are heated only to 200/C. As highlighted in LA-UR-02-2233, many salts condense well above that temperature.

a: At this time, the procedure is vague with regard to exactly what constituents would be considered unacceptable. It may be appropriate for DOE to develop a list of constituents that are considered contaminants of concern for pressurization during long-term storage. Future guidance for the implementation of TGA-FTIR/MS techniques should address the detection of these constituents of concern.