

DEFENSE NUCLEAR FACILITIES SAFETY BOARD

October 20, 1994

MEMORANDUM FOR: G. W. Cunningham, Technical Director
COPIES: Board Members
FROM: J. Kent Fortenberry
SUBJECT: Hanford Plutonium Finishing Plant Interim Actions

1. **Purpose:** This report summarizes interim actions being pursued at the Hanford Plutonium Finishing Plant. This information is based on a facility visit conducted by the Defense Nuclear Facilities Safety Board (DNFSB) technical staff (Fortenberry, Grover, and Gubanc) on October 5-6, 1994, which also included a visit to the K-East Basin.
2. **Summary:** The Plutonium Finishing Plant is awaiting results of an Environmental Impact Statement (EIS) to decide future actions at the facility. In the interim, actions are being taken to address immediate safety concerns and to improve the facility condition. Safety concerns being addressed include stabilizing and repackaging reactive plutonium-bearing material, reducing operator exposure, and verifying container integrity of highly corrosive plutonium solutions. Facility condition improvements being pursued include reducing contamination areas, increasing available glovebox storage capacity, and improving cleanliness and appearance. These interim actions provide an additional benefit of helping to maintain proficiency, morale, and general facility readiness.

Except for the Plutonium Reclamation Facility canyon and most of the gloveboxes, the Plutonium Finishing Plant appeared clean and well kept. Discussion with operators confirmed a sense of pride and ownership in the facility. The interim actions being pursued at the Plutonium Finishing Plant can be contrasted with the K-East Basin, where there is little evidence of efforts to improve the facility condition and readiness while waiting for future actions to be identified.

A significant interim action being pursued at the Plutonium Finishing Plant is the thermal stabilization of plutonium-bearing sludge and residue. Attachment I describes this activity. Specific technical staff observations concerning this sludge stabilization process are included as Attachment II.

3. **Background:** The Department of Energy (DOE) had intended to restart portions of the Plutonium Finishing Plant to stabilize the large inventory of plutonium bearing materials (solutions, sludge, scrap, etc.). However, public input into this proposed stabilization campaign convinced the DOE to change its plans and to prepare an Environmental Impact Statement (EIS) to consider potential future actions. This EIS is due to be completed in August 1995.
4. **Discussion:** Because of the decision to perform an EIS, the Plutonium Finishing Plant was faced with a significant delay in cleanup activities. Rather than wait idly for the

EIS record of decision, several interim actions were developed to address immediate safety issues and to improve the facility condition. These interim activities are using existing resources in planning, engineering and conducting various nuclear materials handling activities. Some of the interim actions are identified below.

Aqueous solutions used during a recent training run (about 1500 liters of less than 1 gram/liter plutonium nitrate - 475 grams Pu total) were diluted and transferred to the Tank Farms. Disposal of this solution reduced the possibility of leakage, operator exposure, equipment degradation due to corrosion, and operator surveillance requirements.

Organic solutions used during a recent training run (about 250 liters) were packaged and sent to the central waste complex. Disposal of this solution reduced corrosion of equipment and the possibility of leakage.

Twenty-seven 10-liter containers of highly corrosive plutonium-bearing chloride-fluoride solutions were x-rayed to confirm inner container integrity. Preparations are nearly complete for transferring this material to the Plutonium Process Support Laboratory for testing. This testing will be used to develop processing alternatives for remaining plutonium and uranium nitrate solutions.

Portions of the facility have been cleaned and decontaminated. The duct level rooms and the tunnel areas have been cleaned of loose smearable contamination and reduced from a Surface Contamination Area (SCA) to a Radiological Controlled Area (RCA). Plutonium bearing duct work is being removed to reduce radiation exposure to plant personnel, to reduce the inventory of seismically dispersible plutonium, and to prepare certain areas for decontamination and decommissioning.

Low plutonium content sludge has been cemented and transferred to the central waste complex. This reduced the number of sludge items and freed storage space for future cleanup activities. In addition, high plutonium content sludge will be stabilized in a furnace and then placed in vault storage. Attachment I discusses this sludge stabilization activity in more detail.

5. **Future Staff Actions:** The DNFSB technical staff will continue to follow activities at the Plutonium Finishing Plant, including the high-plutonium content sludge stabilization. DOE's record of decision from the EIS will of course influence future staff actions.

Attachment I Plutonium Sludge Stabilization

1. **The Need to Stabilize:** The material to be stabilized is reactive and cannot be placed in normal vault storage. Off gassing from the material would likely rupture typical vault storage containers. Stabilization will allow this material to be removed from gloveboxes and stored in the vault. This will reduce operator exposure, free up storage

for additional cleanup activities, improve the security of the material, and move the facility closer to eventual clean out.

2. **The Material to be Stabilized:** About 236 items have been identified for stabilization, representing 400 to 600 furnace loads. A furnace load is limited to 500 grams of material. There are three categories of material that will be stabilized: Plutonium Reclamation Facility (PRF) sludge, plutonium oxycarbonate from the Remote Mechanical C (RMC) Line, and plutonium oxide from the RMC Line.

PRF sludge includes centrifuge sludge, PRF glovebox sludge, and canyon sludge. PRF sludge potentially contains the organic solvent tributyl phosphate (TBP), and will be sampled for organic content. Items with greater than 2% organic content (e.g., TBP) will not be stabilized. None of the items identified for stabilization is expected to contain greater than 2% organic.

RMC Line material consists of miscellaneous floor sweepings which includes plutonium oxide, plutonium oxycarbonate, and plutonium fluoride. RMC Line material could also include plutonium oxalate. However, since plutonium oxalate degrades to plutonium oxycarbonate with a reaction half-life of 64 days, no oxalate is expected (storage time is in excess of four years). The RMC Line materials do not contain TBP. The only test performed on this feed material is to check for plutonium fluoride. The highly corrosive plutonium fluoride, identified by its pink color, will not be fed into the furnace. *Plutonium oxycarbonate* will form an intermediate liquid phase at greater than 100°C. The aqueous portion is driven off by heat and the remaining material is oxidized to plutonium oxide powder.

Plutonium oxide from the RMC Line will also be fed to the furnace. The oxide is simply dried and no chemical reactions are involved.

3. **The Stabilization Process:** Two furnaces, capable of temperatures in excess of 1000°C, have been installed in a glovebox and are controlled from a common control console. The temperature profile for the stabilization process is controlled automatically. Hardwired interlocks have been added to the oven control system to shut off power in the event of high oven temperature, door open, oven temperature deviation from program, high glovebox temperature, and temperature monitor failure.

The primary hazard particular to the stabilization process is the production of flammable butene from the decomposition of TBP. Butene has an autoignition temperature of 324°C. Four barriers have been established to eliminate the potential for a flammable mixture of butene.

- a. Sampling of feed material for organic content (2% organic limit).
- b. Continuous forced offgas from furnace of approximately 120 cfh via the 26-inch vacuum line to prevent buildup of any butene generated.
- c. A 30-35 cfh CO₂ cover gas during the temperature regime where butene could be generated.
- d. A temperature profile that allows TBP to decompose slowly prior to reaching the autoignition temperature of butene.

Three temperature profiles will be used for sludge stabilization, depending on the feed material.

a. For PRF sludge:

1. Temperature is ramped to 175·C over a 0.5 hour period with a CO₂ purge.
2. Temperature is held at 175·C for 1.5 hours with a CO₂ purge to allow decomposition of TBP into butene prior to reaching the autoignition temperature of butene (324 · C).
3. Temperature is ramped to 300·C over a 0.5 hour period.
4. CO₂ purge is secured.
5. Temperature is ramped to 1000·C over a 5 hour period.
6. Temperature is held at 1000·C for 1 hour.
7. Furnace is turned off and allowed to cool to 200·C (5 to 6 hours).
8. Material is placed in desiccator and allowed to cool to 75·C (1 to 2 hours).

b. For RMC Line oxycarbonate:

1. Temperature is ramped to 175·C over a 0.5 hour period.
2. Temperature is held at 175·C for 1 hour to allow time for the free liquid to evaporate without foaming over.
3. Temperature is ramped to 1000·C over a 5.5 hour period.
4. Temperature is held at 1000·C for 1 hour.
5. Furnace is turned off and allowed to cool to 200·C (5 to 6 hours).
6. Material is placed in desiccator and allowed to cool to 75·C (1 to 2 hours).

c. For RMC Line oxide:

1. Temperature is ramped to 1000·C over a 6 hour period.
2. Temperature is held at 1000·C for 1 hour.
3. Furnace is turned off and allowed to cool to 200·C (5 to 6 hours).
4. Material is placed in desiccator and allowed to cool to 75·C (1 to 2 hours).

4. **The Storage Process:** After the material has cooled to less than 75·C, it is removed from the desiccator and ground-up using a mortar and pestle. If necessary, the material will be sieved to remove large pieces. The material is then put into a slip-lid can, which is returned to the desiccator to await additional material. When the slip-lid can is sufficiently full, a sample is taken for Loss-on-Ignition (LOI) analysis to verify that less than 1% volatiles remain. If the LOI result is less than 1%, the slip-lid is taped,

and the slip-lid can is bagged out of the glovebox and in turn packaged in two, contamination free, mechanically sealed food pack cans in accordance with PFP Operating Specifications for Special Nuclear Material Storage.

This sludge stabilization activity is expected to produce approximately 150 containers of Special Nuclear Material for vault storage. After calorimeter and isotopic analysis, these containers will be stored in vault locations equipped with the Vault Safety and Inventory System (VSIS). The VSIS continuously monitors the container's presence, identification number, bottom deflection, and temperature.

5. **Open Issues:** Two items must be resolved prior to starting plutonium sludge drying at PFP: DOE-RL approval of the associated Environmental Assessment (EA) and resolution of the 232Z Unreviewed Safety Question (USQ). Approval authority for the sludge drying activity EA rests with DOE-RL. Approval is expected in October 1994.

The 232-Z USQ deals with an unanticipated amount of seismically dispersible plutonium in the 232-Z incinerator building. Pending resolution, movement of fissile material is severely restricted at the PFP. This USQ must be resolved, or PFP must obtain some relief from the fissile material movement restrictions before significant sludge stabilization can commence.

Attachment II Staff Observations on PFP Plutonium Sludge Stabilization

1. Exposed tubing for the furnace ventilation exhaust stream will be extremely hot while operating (about 750-F). The basis document for sludge stabilization (WHC-SD-CP-OCD-040, R0) notes that "Access to the furnace area inside the glovebox should be severely limited to minimize the chance of contacting the exhaust tubing with gloves." This concern is addressed by the operating procedure for the furnace (ZO-160-032) which requires that gloves be pulled out of the glovebox and secured with elastic cords during the heat up/cool down cycle.

The glove most capable of contacting the No. 1 furnace offgas exhaust tubing, the hottest part of the furnace, is the glove required to valve in the No. 1 ceramic filter delta-P gauge prior to each furnace load. In addition the glovebox to room delta-P is about negative 1.75 inches of water, sufficient to cause the glove to fully extend inside the glovebox. Because of the frequent use of this glove and the tendency for the glove to extend into the glovebox, the observed elastic cord configuration did not appear to provide adequate control of glovebox integrity.

2. The furnace operating procedure (ZO-160-032) directs that material be allowed to cool in the desiccator for 1 to 2 hours in order to reach $\leq 75\text{C}$. In practice, it seems to take closer to a full 2 hours to reach 75C. To meet the intent of this step, a "meat thermometer" is used to measure the temperature of the material in the desiccator. If a temperature measurement is needed, it should be included in the operating procedure. In addition, the "meat thermometer" represents a glove puncture hazard and should be removed or replaced with a more benign device.

3. Processed material is placed in a slip-lid can. This slip-lid can is then stored in a desiccator. Subsequent process runs are added to the can until it is over three-quarters full. At this time a sample is taken for Loss-On-Ignition (LOI) testing. There is no provision in the procedure for homogenizing the contents to ensure a representative sample. As a worst case, only the material just out of the furnace would be used to perform the LOI analysis.
4. The "boat" is fabricated from 1/8 inch wall stainless steel pipe with welded endcaps. The boat is then polished to minimize the adherence of oxides. In addition plastic utensils are used to remove the oxide to prevent marring the finish. However stainless steels become embrittled and suffer extensive scaling at temperatures above 800·C. This problem was addressed for the furnace offgassing line by using Inconel 600. Although the boat was inside an operating furnace and not available for inspection, scale was seen on the floor of the non-operating furnace and on the glovebox floor underneath the furnace door. The boat was described by operators as being black. Oxide adherence to the scaled surfaces of the boat may become a problem.