DEFENSE NUCLEAR FACILITIES SAFETY BOARD
Washington, DC 20004-2901

September 8, 2021

The Honorable Jennifer M. Granholm
Secretary of Energy
US Department of Energy
1000 Independence Avenue, SW
Washington, DC 20585-1000

Dear Secretary Granholm:

The Defense Nuclear Facilities Safety Board (Board) evaluated the technical basis for the May 1, 2019, Carlsbad Field Office (CBFO) letter on evaluating waste containing mixtures of nitric acid or nitrate salts with polysaccharides. This same waste type was involved in the 2014 Waste Isolation Pilot Plant (WIPP) radiological release event that led to a three-year shutdown of the facility. In its letter, CBFO concluded that such waste will not undergo autocatalytic runaway reactions after the waste has been aged for a specified time period. The Board finds that the CBFO letter lacks the technical basis to support that conclusion. The Board's finding is consistent with the conclusions of a Department of Energy-sponsored technical review team assigned to evaluate disposal pathways for the inappropriately remediated nitrate salt waste stored at the Waste Control Specialists facility in Andrews, Texas. As a result, this type of waste may not be acceptable for disposition at WIPP unless additional technical justification is provided, controls are implemented, or the waste is treated.

The enclosure details the Board's assessment of the CBFO letter and supporting reports. The Board is aware that CBFO has identified plans to revise its letter with an amended justification. Pursuant to 42 United States Code §2286b(d), the Board requests that the Department of Energy provide a report and briefing within 90 days of receipt of this letter that describes its plan for safely managing these waste materials across the complex.

Sincerely,

Joyce L. Connery

Joyce L. Connery
Chair

Enclosure

c: Mr. Joe Olencz

ENCLOSURE

Revised Carlsbad Field Office (CBFO) Letter on Evaluating Waste Containing Nitric Acid and Metal Nitrate Salts with Polysaccharides

Summary. The Defense Nuclear Facilities Safety Board's (Board) staff reviewed the CBFO letter, *Revised CBFO Direction for Nitric Acid and Metal Nitrate Salts with Polyol Organic Chemicals and Polysaccharide Sorbing Material for Chemical Compatibility and Basis of Knowledge Criteria Evaluations*, dated May 1, 2019 [1]. Through this letter, CBFO issued direction to Waste Isolation Pilot Plant (WIPP) certified programs regarding the safety of waste containing nitric acid or nitrate salts mixed with polysaccharides. CBFO states that such mixtures are chemically compatible (i.e., not prone to runaway reaction) if they have been aged for a certain length of time.

CBFO's direction was based on two supporting Difficult Waste Team (DWT) reports: DWT-RPT-005, Revision 1, *Safety Evaluation of Nitric Acid Reactions with Polysaccharides* [2], and DWT-RPT-006, Revision 0, *Safety Evaluation of Remediated Nitrate Salt Waste* [3]. The staff concluded that the CBFO letter and supporting DWT reports lack the technical basis on which to eliminate the possibility of an autocatalytic (thermal) runaway reaction from consideration. As a result, this type of waste may not be acceptable for disposition at WIPP unless additional technical justification is provided, controls are implemented, or the waste is treated.

Background. Transuranic waste containing mixtures of incompatible oxidizing materials and organics pose potential hazards at Department of Energy (DOE) facilities. The 2014 WIPP radiological release event was a result of a chemical reaction between organic kitty litter (a polysaccharide-based material) and nitrate salts in the waste that led to the failure of the drum (this waste is known as "inappropriately remediated nitrate salt [RNS]" or RNS waste). Since the WIPP event, Los Alamos National Laboratory (LANL) has treated a portion of the remaining RNS waste to reduce the reaction hazard and ensure compatibility. However, more than 100 untreated drums are currently stored at the Waste Control Specialists facility in Andrews, Texas, awaiting final disposition. Additionally, DOE's waste can include other mixtures of nitric acid with polysaccharides; for example, LANL's plutonium operations continue to use cheesecloth (i.e., polysaccharide) with nitric acid and heat source plutonium.

At the request of CBFO, LANL-Carlsbad Operations developed two reports to establish a technical basis for CBFO to conclude that waste containing nitrate material mixed with polysaccharides would not likely result in an autocatalytic runaway reaction after a specific aging time (i.e., latency period). On May 1, 2019, CBFO sent a letter to its certified waste programs regarding chemical compatibility and basis of knowledge evaluations for waste mixtures containing nitric acid or nitrate salts and polysaccharides. Based on the DWT reports, CBFO concluded that nitric acid or nitrate salt mixtures with polysaccharides would not undergo autocatalytic runaway reactions after aging beyond the latency periods of 200 days for cellulosic material and 730 days for RNS waste. CBFO further stated that the average daily temperatures

during the aging time must be 50°F or higher in order to ensure the conditions for such a reaction are met. For the purpose of chemical compatibility and basis of knowledge evaluations, the certified waste programs can consider that mixture acceptable without further evaluation. The Board's staff is aware that CBFO has identified plans to revise its direction letter with an amended justification.

Discussion. The CBFO letter authorizes the certified waste programs to evaluate aged waste for chemical compatibility and basis of knowledge criteria while discounting the incompatibility of nitric acid or nitrate salts with polysaccharide materials. In simple terms, CBFO believes that if a waste container has not had a runaway reaction by the end of the aging time, then it does not have the potential for such a reaction. The staff's evaluation of the technical basis for the associated DWT reports identified the following concerns:

1. **Aging time.** The DWT reports derived aging times—after which, the waste is considered chemically compatible—by searching for historical incidents, locating the incident with the longest known (or estimated) duration between mixing the chemicals and the ensuing thermal event, and multiplying by a safety factor of 10. For cellulosic materials, the required aging time is 200 days based on an event at Hanford in 1951. For starch-based materials, the required aging time is 730 days based on the 2014 WIPP radiological release event. The aging times are entirely empirical with a significant reliance on a single selected data point. While the DWT reports discuss fundamental chemical and engineering concepts, there is little linkage between those concepts and the aging times. Caution should be used with such an empirical approach.

   Another area for additional consideration is changes in conditions, such as changes in environmental conditions, changes in the waste configuration, or blockage of the drum vent pathway. CBFO acknowledges that a runaway reaction could still occur if the waste is exposed to the elevated temperatures of a fire. CBFO should explicitly address whether other changes in conditions could lead to a rapid reaction, even after the required aging time has been met.

2. **Threshold temperature.** CBFO believes that an aged waste container is not capable of a runaway reaction, if one did not already occur during the aging time. This assumption would be invalid if the waste was aged at cold temperatures, which suppress reaction rates. Accordingly, the CBFO letter indicates that the average daily temperature needs to be at least 50°F to count a particular day toward the latency period. The DWT reports used 50°F because LANL had previously used a threshold temperature of 50°F for RNS waste. However, LANL was using this temperature for the opposite reason (i.e., to ensure suppression of chemical reactions) and it included some safety margin in deriving the 50°F value [4]. For CBFO's purposes, it would be necessary to include margin in the other direction, resulting in a threshold temperature higher than 50°F. Thus, the 50°F value does not have a strong technical basis backed by modelling, experimental testing, or sampling.

3. **Peer-review process.** The peer review process was applied to DWT-RPT-005, but not DWT-RPT-006. The peer review process also relied heavily on spot checks of the original work rather than a thorough independent verification of the original work through a scientific review process. Therefore, the staff team has concerns with the scope and rigor of the peer review process and whether peer reviewer comments were adequately resolved.

Conclusion. Given the degree of uncertainty highlighted above, the CBFO letter and associated DWT reports lack the rigor and sufficient technical basis to support the conclusion that nitric acid or nitrate salts with polysaccharides waste will not undergo autocatalytic runaway reactions after the aging requirements are met. The safety assumptions being asserted by CFBO are not supported with adequate technical justification. This waste may continue to pose a risk of an autocatalytic runaway reaction or other energetic chemical event beyond the latency period or at an elevated temperature (e.g., fire). The staff team's conclusion is consistent with those outlined by a DOE-sponsored technical review team (TRT) assigned to evaluate disposal pathways for RNS waste stored at the Waste Control Specialists (WCS) facility in Andrews, Texas [5]. "Based on its evaluation, the overarching conclusion of the WCS TRT is the WCS containing RNS waste (WCS RNS) drums have become more stable over time with respect to nitric acid reactions but that existing data are insufficient to completely eliminate the potential of reactions leading to thermal runaway of WCS RNS though actions can be taken to reduce the likelihood of such an event." As a result, this waste may not be acceptable for disposition at WIPP unless additional technical justification is provided, controls are implemented, or the waste is treated.

References

[1] Department of Energy, Carlsbad Field Office, Todd Shrader to Bruce Covert and John C. McCoy, *Revised CBFO Direction for Nitric Acid and Metal Nitrate Salts with Polyol Organic Chemicals and Polysaccharide Sorbing Materials for Chemical Compatibility and Basis of Knowledge Criteria Evaluations*, May 1, 2019.

[2] Los Alamos National Laboratory-Carlsbad Operations, *Safety Evaluation of Nitric Acid Reactions with Polysaccharides*, DWT-RPT-005, Revision 1, January 23, 2019.

[3] Los Alamos National Laboratory-Carlsbad Operations, *Safety Evaluation of Remediated Nitrate Salt Waste*, DWT-RPT-006, Revision 0, April 15, 2019.

[4] Los Alamos National Laboratory, *Chemical Reactivity and Recommended Remediation Strategy for Los Alamos Remediated Nitrate Salt (RNS) Wastes*, LA-UR-15-22393, April 2, 2015.

[5] Savannah River National Laboratory, *Waste Control Specialists Technical Review Team Report***,** SRNL-RP-2020-00146, July 2020.