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**DEFENSE NUCLEAR FACILITIES
SAFETY BOARD**

Washington, DC 20004-2901



January 19, 2024

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

Dear Secretary Granholm:

The Defense Nuclear Facilities Safety Board (Board) has reviewed the chemical compatibility program developed by National Nuclear Security Administration (NNSA) at Los Alamos National Laboratory (LANL). The site uses this program to evaluate the chemical compatibility of radioactive wastes generated at nuclear facilities. Performing this evaluation is a new safety requirement for waste generator sites in U.S. Department of Energy (DOE) Standard 5506-2021, *Preparation of Safety Basis Documents for Transuranic Waste Facilities*. The new safety requirement is a result of lessons learned from the February 2014 accident that shut down the Waste Isolation Pilot Plant for an extended period.

NNSA's development of a formal program to evaluate the chemical compatibility of radioactive waste and its plans to upgrade its safety bases to implement DOE Standard 5506-2021 are important steps toward improving the safety posture at both LANL and the Waste Isolation Pilot Plant. The Board encourages DOE to ensure that other defense nuclear facilities that process, handle, or store transuranic waste implement DOE Standard 5506-2021 expeditiously and develop similar chemical compatibility programs. The enclosed report contains additional details of the notable practices of and suggestions for improvements to the LANL chemical compatibility evaluation program for your information and use.

Sincerely,

Joyce L. Connery
Chair

Enclosure

c: Mr. Ted Wyka
Mr. Joe Olencz

DEFENSE NUCLEAR FACILITIES SAFETY BOARD

Staff Report

October 16, 2023

Review of the Chemical Compatibility Program for Transuranic Waste at National Nuclear Security Administration Facilities at Los Alamos National Laboratory

Summary. The Department of Energy (DOE) has experienced multiple events in the past decade that resulted in significant radiological releases from waste containers. One occurred in February 2014 at the Waste Isolation Pilot Plant (WIPP) and another in April 2018 (involving independent chemical reactions in four separate drums) at the Idaho National Laboratory (INL). In response to these events, the Defense Nuclear Facilities Safety Board (Board) evaluated how DOE analyzes chemical compatibility hazards and implements safety-related controls at facilities that generate, process, and store nuclear waste.

In September 2020, the Board issued Technical Report 46, *Potential Energetic Chemical Reaction Events Involving Transuranic Waste at Los Alamos National Laboratory* (Tech-46). This report identified that “safety bases for both National Nuclear Security Administration and Environmental Management facilities at Los Alamos National Laboratory do not consistently or appropriately consider a potential energetic chemical reaction involving transuranic waste.”

DOE strengthened its safety requirements in this area by issuing a revision to DOE Standard 5506, *Preparation of Safety Basis Documents for Transuranic Waste Facilities*, in August 2021. Among the new requirements is a provision that states, “The hazard analysis shall include an evaluation of the chemicals potentially in the waste to consider whether adverse chemical reactions could occur.”

In response to Tech-46 and DOE Standard 5506-2021, Triad National Security, LLC (Triad), the management and operating contractor for National Nuclear Security Administration (NNSA) facilities at the Los Alamos National Laboratory (LANL), developed a method to evaluate the chemical compatibility of transuranic waste generated from various operational processes.

The staff team reviewed Triad’s chemical compatibility program and found that:

- Triad has implemented several notable process upgrades that reduce the risk of radiological releases that could be caused by adverse chemical reactions in transuranic waste.
- Triad has not yet defined the interface between its safety bases and the chemical compatibility evaluations (CCE). As a result, it is unclear how Triad will upgrade its safety bases to: (1) identify and evaluate specific chemical reactions in waste, (2) estimate the consequences from chemical reactions in waste, and (3) determine

whether safety-related controls need to be identified to protect the worker and off-site public from high consequence events.

- Triad’s CCE process could be improved in several areas, including:
 - Revising the CCEs to clearly describe the methods, assumptions, and references used, such that the CCEs are reviewable and maintainable;
 - Ensuring that any safety-related controls relied upon by the CCEs are implemented (i.e., required per procedure) and are effective at preventing or mitigating an adverse chemical reaction event;
 - Documenting the technical basis for excluding materials from further evaluation in the CCE (e.g., chemicals used in incidental quantities);
 - Developing a process to identify and evaluate changes to the ingredients of commercial off-the-shelf items;
 - Acknowledging the limitations of the CCE methodology in CCE reports and considering development of improvements to the CCE methodology; and
 - Updating the Plutonium Facility (PF-4) documented safety analysis (DSA) to ensure it accurately reflects the chemicals currently used in processes.

Background. Over the past decade, DOE experienced multiple significant events—one in February 2014 at WIPP and another in April 2018 (involving independent chemical reactions in four separate drums) at INL—in which waste drums released radiological materials due to energetic chemical reactions involving the waste [1] [2] [3]. As a result, the Board evaluated how DOE analyzes chemical compatibility hazards and implements controls at facilities that generate, process, and store nuclear waste.

In September 2020, the Board issued Tech-46 [4]. This report identified that “safety bases for both National Nuclear Security Administration and Environmental Management facilities at Los Alamos National Laboratory do not consistently or appropriately consider a potential energetic chemical reaction involving transuranic waste.” Specifically, Tech-46 stated:

- “**Hazard analyses** lack systematic evaluations of the chemical compatibility of transuranic waste streams. These analyses are needed to fully identify potential chemical reaction hazards associated with waste constituents.
- “**Accident analyses** are not bounding, assume inappropriate initial conditions, and do not defensibly estimate the quantity of radioactive material that may be released due to an energetic chemical reaction. As such, additional credited safety-related controls may be necessary to protect workers and the public.
- “Some facilities store transuranic waste without any engineered controls beyond the

waste container. The radiological release events that occurred at the WIPP and INL demonstrated the importance of incorporating **multiple layers of protection** to reduce the consequences of an accident.”

DOE strengthened its requirements in this area by issuing a revision to DOE Standard 5506 in August 2021 [5]. Among the new requirements is a provision that states, “The hazard analysis shall include an evaluation of the chemicals potentially in the waste to consider whether adverse chemical reactions could occur.” DOE and its contractors that operate transuranic waste facilities have been discussing implementation approaches for the newly revised standard. Triad plans to implement the revised standard for the PF-4 DSA within the next year.

In response to Tech-46 and DOE Standard 5506-2021, Triad developed a method to evaluate the chemical compatibility of transuranic waste generated from its various operational processes. This evaluation will help ensure that no adverse reactions will occur between different chemical components in the waste. These CCEs identify all chemicals used in a specific process at each NNSA-owned LANL facility and then evaluate combinations of these chemicals that can end up in the waste by using a methodology outlined in EPA-600/2-80-076, *A Method for Determining Compatibility of Hazardous Waste* [6]. The EPA methodology was developed in 1980 and evaluates the compatibility of binary combinations of materials. Triad enters the new information process for each completed CCE to determine whether an unreviewed safety question (USQ) exists. No positive USQ determinations have yet resulted from Triad’s CCE development.

Separately, the Central Characterization Project (CCP), a different entity overseen by the DOE Carlsbad Field Office rather than Los Alamos, also performs CCEs on waste at LANL. CCP is responsible for safety at WIPP, while Triad is responsible for the safety of NNSA’s facilities at LANL. Prior to shipments of waste to WIPP, CCP must develop a CCE for the waste to ensure chemical compatibility. Both Triad and CCP use the methodology outlined in EPA-600/2-80-076. However, CCP CCEs simultaneously analyze waste produced by several operational processes, while the Triad CCEs only analyze one process at a time.

The staff team has three broad observations from its review of Triad’s chemical compatibility program, related to: (1) implementation of notable process upgrades; (2) the interface between safety bases and CCEs; and (3) potential improvements to the CCE process.

Process Upgrades. Over the past few years, Triad has implemented several notable process improvements that reduce the risk of radiological releases caused by adverse chemical reactions in transuranic waste. These upgrades include the following:

Documented Safety Analysis Update—Triad is in the process of developing a new PF-4 DSA [7] that will meet the guidance and requirements in DOE Standard 3009-2014, *Preparation of Nonreactor Nuclear Facility Documented Safety Analysis* [8], and DOE Standard 5506-2021. This effort is expected to finish in fiscal year 2024.

Process-specific CCEs—In response to Tech-46 and DOE Standard 5506-2021, Triad has begun developing comprehensive CCEs for all radioactive waste generating processes at its

LANL facilities. Triad is one of the first DOE contractors at a generator site to develop process-specific CCEs, which will improve the safety of operations that generate radioactive waste. To date, Triad has completed CCEs for all the waste generating processes at PF-4 and is working to complete CCEs for the remaining Triad facilities at LANL. The CCEs identify potential adverse reactions that could occur in waste and allow Triad to identify controls to prevent or mitigate these reactions.

Configuration Control of Chemical Absorbents—Triad has developed a specific process to ensure configuration control of chemical absorbents. When an operator needs to absorb transuranic liquids to create WIPP-compliant waste, they must follow PA-DOP-01665, *Characterization and Absorption of Liquids* [9]. This procedure requires a hazardous waste management acceptable knowledge specialist (AKS) to evaluate the compatibility of the liquid, sorbent, and packaging, and recommend a specific absorbent and quantity of absorbent to be used. The AKS then observes the transuranic liquid being absorbed. This improvement will help prevent non-compliant absorbents from being used within waste. If this control had been in place earlier, it may have prevented the 2014 WIPP event [1], which was caused in part by the use of an inappropriate absorbent.

Integration of Waste Management Specialists with Operational Processes—Triad has better integrated AKS personnel with operational processes. Specifically, AKS personnel perform annual walkdowns of each process and must review all process and procedural changes. Further, Triad has a dedicated acceptable knowledge technologist for each process. This integration will help ensure that potential hazards are properly analyzed and controlled.

New Procedural Control—Triad has implemented a new procedural control that ensures materials that originate from an inert glovebox spend at least seven days in an air environment before being disposed of as waste. This control helps ensure that any materials that are potentially reactive with air will complete such reactions before being disposed of as waste, especially for fines that are directly exposed to air. This control was developed in response to a February 2021 event in which Triad personnel observed sparks emanating from a waste drum attached to a glovebox [10]. Personnel were emplacing waste items into the drum as part of a drum-out evolution. The sparks were caused by unreacted titanium metal fines that had been removed from an inert glovebox and were being disposed of as waste in an air glovebox.

Procurement of Real-Time Radiography Trailer—Triad has procured a new real-time radiography trailer for placement at the Transuranic Waste Facility to improve its ability to analyze waste containers. Triad expects to have this trailer operational within the next few years.

Interface between CCEs and Documented Safety Analyses. Triad has not yet defined what the interface between facility safety bases and CCEs will be. As a result, the staff team could not determine how Triad will: (1) comprehensively identify chemical hazards in the waste, and (2) perform a DSA hazard evaluation (including evaluation of consequences) for potential chemical reactions in waste. As a result, it is unclear what, if any, controls will be designated as safety-related to prevent or mitigate potential chemical reaction events in waste.

Hazard Identification—DOE Standard 3009-2014 states that the “methodology used for hazard identification shall ensure comprehensive identification of the hazards.” Triad’s CCEs identify potential chemical reactions that, in the absence of controls, could lead to adverse consequences. However, these reactions are not specifically listed in the PF-4 DSA hazard identification section. In other words, there is currently no formal link between CCEs and the PF-4 DSA. Without this link, it is not yet clear how Triad will ensure that the DSA’s hazard identification is comprehensive.

Hazard Evaluation Events—As part of its PF-4 DSA upgrade effort, Triad is developing a method for determining when specific chemical reactions should be evaluated as a unique hazard event in the DSA instead of being captured as part of a generic chemical reaction event. Analyzing specific reactions can be important for understanding the unmitigated consequences for those reactions and for identifying whether safety-related controls are needed for that scenario. The hazard evaluation in the PF-4 DSA [7] currently lists a few events that are tied to a specific chemical reaction, such as SW-2-002 (reaction of polysaccharides and nitric acid). The hazard evaluation also has events such as SW-3-003 (chemical decomposition of waste) that broadly apply to unspecified chemical reactions. Both the specific and the generic events play an important role in the hazard evaluation.

It is important to note that DOE Standard 3009-2014 has a process for screening some chemicals from the hazard analysis. However, chemicals that “have the potential to be an accident initiator involving radioactive or hazardous material releases...are retained as part of the DSA hazard evaluation.” Accordingly, all incompatible chemical combinations that can cause a release of radioactive materials from a waste container are required to be analyzed in the DSA.

Consequence Determination—When Triad integrates the CCE into the safety basis, it will need to determine the unmitigated consequences of different reaction scenarios. Chemical reactions can lead to different outcomes, ranging from cases with no radiological release to over-pressurizations with large releases. When analyzing over-pressurization events involving finely divided waste, DOE Standard 5506-2021 lists several airborne release fraction (ARF) and respirable fraction (RF) values depending on the release pressure. However, the standard does not provide guidance for determining how much pressure a given chemical reaction would cause in a waste container. As a result, selecting appropriate and bounding ARF and RF values for chemical reactions involving finely divided waste requires careful consideration. Triad has not yet determined how it will select specific ARF and RF values when performing the unmitigated consequence analysis for specific adverse chemical reaction events.

Safety-related Control Selection—In its CCEs, Triad assumes procedural controls are in place and function to prevent or mitigate adverse chemical reactions. For example:

- The Analytical Chemistry Laboratory (ACL) CCE [11] assumes that absorbed acids are dried and/or neutralized prior to being disposed of as waste to rule out potential adverse chemical reactions.
- The impact test facility CCE [12] lists a trinitrotoluene (commonly known as TNT) based propellant as a unique hazard. While not explicitly documented in a CCE,

Triad personnel stated that this highly reactive material is screened out of the CCE because the hazard would be recognized by operators per their operating procedure and would not end up in the waste.

- While not explicitly documented in a CCE, Triad stated that (per the new procedural controls mentioned above) materials that originate from an inert glovebox are placed in an air glovebox for at least seven days prior to waste packaging to reduce the likelihood of adverse interactions with air after packaging as waste [13].

Given that Triad is relying on such controls to avoid adverse chemical reactions, the controls should be considered in the DSA hazard evaluation. If the unmitigated consequences of an event are found to be high, then safety-related controls would need to be identified for those events.

Opportunities to Improve Triad’s CCE Program. During its review, the staff team identified several opportunities for improving Triad’s CCE program, as documented below:

Formality of CCEs—Triad’s CCEs are not formally documented. Specifically, Triad’s CCEs do not include the purpose and scope of the evaluations, the methods and assumptions used to generate the evaluations, report titles, revision numbers, signatures, or references. For example, Triad’s CCE reports do not mention that they apply the methodology from EPA-600/2-80-076. Triad’s CCE reports also do not mention key assumptions, such as the fact that Triad assigned the same reactivity group numbers (RGN) and material quantities as assumed in CCP’s CCEs [14]¹. As another example, Triad’s CCEs use the term “debris” without explaining the meaning of the term. Triad personnel verbally explained that “debris” in a CCE represented a group of materials that was assumed to be present in all processes.

Overall, there is not enough information in Triad’s CCEs for a reader to determine how the analysis was performed and how conclusions were developed. While Triad provided the needed context to the staff team verbally, better documentation is needed to ensure that CCEs are enduring, reviewable, and maintainable. Triad personnel indicated that they would consider revising CCEs in the future to be more formal.

Technical Justification in CCEs—Triad’s CCEs have a technical justification section that explains why a potential chemical reaction will not have adverse effects. These technical justifications list several assumptions that are not adequately supported. For example, the ACL CCE [11] assumes that operators will take certain actions in response to spills of hydrochloric and hydrofluoric acid: “Incidental spills of hydrochloric and hydrofluoric acids are sorbed onto non-polysaccharide wipes, and operators demonstrate that wipes that potentially came into contact with hydrochloric acid and hydrofluoric acid are dry prior to disposal via dual independent verification that is documented and signed.” However, the facility’s procedures do not require those specific actions for spills of those acids. Triad personnel informed the staff team that there are “no requirements for these chemicals to be sorbed on non-polysaccharide

¹CCP has developed several CCEs to support characterization of waste at LANL; Reference 14 is an example of these CCEs.

wipes....” This discrepancy was discussed during the staff team’s interaction, and Triad personnel stated they would consider how to address this inconsistency in a future revision.

As another example, the ACL CCE states, “Actions to the waste during packaging efforts include taping the terminals of all batteries to limit the possibility of caustic leaking.” While this is a best practice for preventing short circuits or sparking, taping the terminals would not prevent batteries from leaking and potentially causing an adverse reaction. The staff notes that the ACL CCE also states that the relative quantities and concentration of chemicals present from a battery in the waste stream would be insufficient to result in an adverse reaction. However, the reference² cited in the ACL CCE [15] asserts, “It is possible that caustic electrolytes (RGN 10) could leak in incidental quantities insufficient to result in an adverse reaction consequence,” but does not provide any technical evidence to support screening out batteries.

Chemical Quantities—As noted earlier, when developing their own CCEs, Triad personnel relied on CCP’s CCEs to determine the quantity of chemicals that could end up in a waste container. Accordingly, if CCP’s analysis determined that a chemical was used in “incidental” quantities and could be excluded from analysis, so did Triad’s. The Triad analysis did not provide technical justification for why any given chemical was deemed incidental, and therefore excluded from analysis.

- A commercially available cleaning spray is used throughout PF-4, but it is considered incidental in the CCEs and not further analyzed. Triad personnel clarified that they considered the cleaning spray to be “incidental” because most of the material evaporates. However, some non-volatile residue would remain. The CCEs do not provide a basis for whether a RGN should be assigned to the residues. Note that the staff team is using this specific cleaning spray as an example and is not suggesting that it is hazardous.

Some processes only require small amounts of certain chemicals, and those chemicals are not further analyzed in the CCE. However, the storage container for these chemicals may be large. DOE Standard 3009-2014 calls for the evaluation of normal, abnormal, and accident conditions. Thus, there should be consideration of off-normal situations, such as spills of larger quantities that end up in radiological waste, or circumstances where operators use more of a chemical than is typical. If the presence of a chemical in a higher-than-usual amount could cause significant consequences, that is something that should be identified, understood, and controlled.

Triad personnel stated that they typically only introduce the required amount of a process chemical into a glovebox instead of introducing large quantities and then using only a subset of that material. Further, a waste questionnaire is filled out for each waste drum, and this questionnaire would record any abnormal events (such as a spill). Triad analysts would then evaluate whether the existing CCE was applicable to the waste, and if not, they would perform a new analysis. Finally, the visual examination and visual inspection processes compare the materials that will end up in a waste container against the CCE and could determine whether a

² The ACL CCE states, “See correspondence from CCP, May 05, 2022.” The CCE does not have a formal reference list that includes a document title to allow an independent reviewer to determine what this reference is. Triad subsequently provided reference [15] as the basis after further discussions with the staff.

material was appropriately analyzed. While these are good practices that can help mitigate concerns related to unanalyzed chemicals, there should still be conservative decision-making regarding the categorization of chemicals as “incidental” and whether procedural controls need to be elevated to safety-related controls to prevent high consequences during off-normal circumstances.

Overall, the DSA should consider whether abnormal conditions, including spills or other errors, could lead to generation of waste containing incompatible chemicals. If a CCE for the waste does not consider this possibility, then the DSA needs to analyze such events. Triad personnel stated that in future revisions to the CCE, they planned to document the technical justification for why various chemicals could be excluded from analysis.

Changes to Commercial Products—Triad does not have a formal process for identifying and evaluating changes to ingredients in commercial off-the-shelf products. For example, cleaning spray (discussed previously), commercial soap, and proprietary absorbents are used in PF-4. If the vendor changes the ingredients of one of these products, it may not notify Triad. In 2019, the proprietary formula for the soap used at PF-4 was changed. While Triad identified this ingredient change, it may not identify all ingredient changes to commercial off-the-shelf products without a formal process in place. Triad personnel stated that they would consider how to evaluate commercial off-the-shelf products going forward, including whether to add requirements to Triad’s procurement system.

Limitations of Methodology—Triad’s process-level CCEs have several limitations that are not acknowledged in its CCE reports. Some examples of limitations include:

- The CCEs use a methodology published by the EPA [6] to identify incompatible combinations of chemicals. The EPA document says it assumes that the “chemicals react at ambient temperature and pressure.” The document does not define what it meant by “ambient,” though it presumably does not apply to fire conditions.
- Using the EPA methodology, the CCEs only consider interactions between pairs of chemicals. However, adverse reaction events can involve a complex sequence of reactions, with the overall consequences being more severe than the consequences of any one reaction involving two chemicals. For example, LANL researchers who studied the 2014 WIPP event found that the event may have initiated with unspecified “low-level chemical reactions,” followed by a series of reactions [16]. “Trace-metal impurities” may have also played a role. The Idaho Cleanup Project team that investigated the 2018 drum over-pressurization reactions at Idaho National Laboratory also found that a sequence of reactions may have occurred [2].
- While DOE Standard 5506-2021 recommends analysis of “slow reactions as the waste ages,” the CCEs do not explicitly consider how waste may chemically or physically change over time (e.g., peroxide-forming chemicals, eventual desorption of adsorbed liquids).

- Application of the EPA methodology may not identify all hazards involving chemicals. For example, the method will not necessarily identify pyrophoric materials. As another example, aqua regia is a fuming liquid mixture of nitric acid (RGN 2) and hydrochloric acid (RGN 1). The EPA document's matrix does not report gas generation as a hazard for a combination of RGNs 1 and 2. While this example may not be relevant to transuranic waste, it demonstrates that the EPA method by itself will not identify the hazards of all interactions.
- The EPA methodology does not evaluate the effects of ionizing radiation on chemical reactions and chemical species present in the waste.

Outdated Information in the PF-4 DSA—The PF-4 DSA [7] lists several hazardous chemicals as being involved in analytical chemistry operations, including hydroxylamine nitrate, acetone, and xylene. However, the ACL CCE [11] does not include analysis of these chemicals. Triad personnel stated that they evaluated the process procedures and found that these chemicals are no longer used. Triad should update the DSA to ensure it reflects current processes.

Conclusion. The staff team reviewed Triad's chemical compatibility and found that:

- Triad has implemented several notable process upgrades that reduce the risk of radiological releases caused by adverse chemical reactions in transuranic waste.
- Triad has not yet defined the interface between its safety bases and CCEs. As a result, the staff could not determine how Triad will upgrade its safety bases to: (1) identify and evaluate specific chemical reactions in waste, (2) estimate the consequences from chemical reactions in waste, and (3) determine whether safety-related controls need to be identified to protect the worker and off-site public from high consequence events.
- Triad's CCE process could be improved in several areas, including:
 - Revising the CCEs to clearly describe the methods, assumptions, and references used, such that the CCEs are reviewable and maintainable;
 - Ensuring that any safety-related controls relied upon by the CCEs are fully implemented (i.e., required per procedure) and are effective at preventing or mitigating an adverse chemical reaction event;
 - Documenting the technical basis for excluding materials from further evaluation in the CCE (e.g., chemicals used in incidental quantities);
 - Developing a process to identify and evaluate changes to the ingredients of commercial off-the-shelf products;
 - Acknowledging the limitations of the CCE methodology in the CCE reports and considering developing improvements to the CCE methodology; and

- Updating the PF-4 DSA to ensure it accurately reflects the chemicals currently used in processes.

References

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