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DEFENSE NUCLEAR FACILITIES SAFETY BOARD

Washington, DC 20004-2901



March 12, 2019

The Honorable James Richard Perry Secretary of Energy US Department of Energy 1000 Independence Avenue, SW Washington, DC 20585-1000

Dear Secretary Perry:

On April 11, 2018, four waste drums at the Idaho National Laboratory underwent overpressurization, ejecting their lids and spreading radiological waste within a facility. The Department of Energy has found that waste in the drums generated methane gas, which contributed to the event. The Defense Nuclear Facilities Safety Board has identified two safety items related to hazards posed by methane-generating wastes, as detailed in the attached report. In particular, current or future drums with repackaged waste may contain flammable gases in high enough concentrations to allow deflagrations. DOE does not have effective controls at the Idaho National Laboratory to prevent or mitigate such deflagrations.

The Board continues to collect information and evaluate the safety implications of the April 2018 over-pressurization event, both at Idaho National Laboratory and across the Department's weapons complex. As part of this effort, the Board intends to conduct a public hearing on the subject of safety management of solid waste storage and processing in the complex by May 2019.

Pursuant to 42 U.S.C. § 2286b(d), the Board requests a response and briefing, including analysis or supporting data, to the following questions within 45 days of receipt of this letter:

- Does the Department plan to use its Corporate Operating Experience Program to alert other sites to this issue, to gauge the potential for occurrence of this type of event, and to take steps to prevent such an occurrence?
- Has the Department conducted an assessment to determine if INL and other defense nuclear facilities have product drums that have not had their flammable gas concentrations measured?
- What is the Department's schedule for measuring the flammable gas concentrations in untested product drums at INL, and what is the safety strategy for such drums that are found to be flammable or near-flammable?

- Has the Department identified any vented drums, beyond those listed in this report, at defense nuclear facilities that were sampled and found to have flammable or near-flammable conditions?
- Has the Department identified other defense nuclear facilities that have, or could have, solid wastes that include metal carbides?
- While the Department is revising DOE Standard 5506, how does it plan to address the deficiencies in that standard in the short-term?

Yours truly,

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Bruce Hamilton Chairman

Enclosure

c: Mr. Joe Olencz

DEFENSE NUCLEAR FACILITIES SAFETY BOARD

Staff Report

December 10, 2018

Idaho Waste Drums with Elevated Methane Concentrations

Summary. On April 11 and 12, 2018, an event occurred at a building known as Accelerated Retrieval Project (ARP) V, at the Idaho National Laboratory (INL). Four drums containing solid radioactive waste underwent over-pressurization. The drum lids were ejected, and radiological material was spread within ARP-V. The Department of Energy's (DOE) Idaho Operations Office (DOE-ID) is responsible for ARP-V, and Fluor Idaho, LLC (Fluor Idaho) is the contractor that operates the facility.

In the course of investigating the causes of the event, Fluor Idaho learned that material from the event drums was generating methane, a flammable gas. If DOE and Fluor Idaho do not properly control this flammable gas hazard in other drums where it may exist, such drums could undergo over-pressurizations or deflagrations, causing a release of radiological materials.

This report documents the Defense Nuclear Facilities Safety Board's (Board) staff team's assessment of the flammable gas hazard and the current controls that DOE-ID has in place. The staff team learned of instances at INL where waste drums have contained methane at flammable concentrations, despite being vented¹. Those cases demonstrate that a flammable condition in a vented drum is a credible scenario that should be analyzed, with controls to prevent or mitigate deflagrations. The staff team found that DOE-ID lacks controls to prevent the creation of new drums with elevated concentrations of methane. Further, once waste is repackaged into a drum, DOE-ID has no requirement for measuring the flammable gas concentration in the drum in a timely manner. While personnel eventually do take such a measurement before shipping drums to the Waste Isolation Pilot Plant (WIPP), this measurement might not take place for months, if not longer. If a drum is flammable but facility personnel are not aware of this condition, then facility personnel would not be able to take additional precautionary or protective measures. Even if facility personnel were aware that a drum was flammable, they have no formal procedure for taking such precautions. Also, methane concentrations may vary in complex ways over time, so a single measurement may not necessarily be indicative of the hazard in that drum. Finally, many drums are staged in buildings that do not have confinement ventilation systems to filter contamination from the air before it leaves the building. Thus, the staff team concludes that DOE-ID lacks effective controls to prevent or mitigate deflagrations in drums of repackaged waste

To obtain the information for this report, the staff team held discussions with DOE-ID and Fluor Idaho personnel on September 25-26, October 29, and November 7, 2018.

¹ The staff team recently learned that there have also been vented drums at INL with flammable concentrations of hydrogen. The staff team is still collecting information about these drums.

The deflagration hazard posed by methane is the prime focus of this report, though Fluor Idaho does not believe a deflagration occurred in the April event. DOE-ID has recognized the deflagration hazard (discussed further below). The staff team is continuing to evaluate other topics related to the April 2018 event.

Background. ARP-V is a tensile-membrane building that is part of the Radioactive Waste Management Complex (RWMC). There have been a series of ARP structures at RWMC. The primary mission of the ARPs is to provide an enclosure for the exhumation and repackaging of waste from the subsurface disposal area (SDA) at the RWMC. After Fluor Idaho repackages the waste into new drums at RWMC, it stores those product drums in a storage enclosure at RWMC and at a neighboring facility, the Advanced Mixed Waste Treatment Project (AMWTP), until they can be disposed.

DOE-ID and its contractors also sometimes repurpose an ARP for another mission. At the time of the event, Fluor Idaho was using ARP-V to examine and repackage wastes that were initially exhumed from the SDA in the 1970s. This work is part of the Sludge Repackaging Project (SRP). Fluor Idaho was conducting this activity to support eventual shipment of the waste to disposal sites such as WIPP.

The staff team reviewed the exhumation and sludge repackaging in the ARPs, and the hazards associated with the product drums created from those activities.

Role of Methane in the April 2018 Event—Fluor Idaho collected samples of the material involved in the April 2018 event, and sent them to off-site laboratories for analysis. The laboratory results showed that the samples were emitting methane, especially when the temperature of the samples was raised. Fluor Idaho developed a hypothesis that the source of the methane was a hydrolysis reaction between water and beryllium carbide, and possibly also uranium carbide [1]. The staff team found through a literature search that beryllium carbide can react at room temperature with humidity in the air [2, 3], but these references do not provide quantitative information on the rate of the reaction under these conditions.

Fluor Idaho's causal analysis report [1] describes the generation of methane as possibly contributing to the event, but as a secondary reaction. The report identifies the oxidation of uranium metal in the waste as the initiating reaction that provided the heat for the secondary reactions. According to Fluor Idaho's hypothesis, the secondary reactions generated gases that caused a mechanical over-pressurization, i.e., the gases over-pressurized the drum without undergoing ignition and deflagration². Fluor Idaho recently has prepared a technical report [4] with more detailed discussions of these chemical reactions. At the time of this staff report, the staff team had not yet reviewed Fluor Idaho's technical report.

Different Accident Scenarios and Missed Opportunities—This staff report mainly focuses on the possibility of methane deflagrations in current and future operations, even though Fluor Idaho does not believe a methane deflagration occurred in the April 2018 event. When drawing lessons learned, it is important to consider all potential hazards highlighted by the event, and not

² There is a clarifying discussion on the terms 'deflagration' and 'over-pressurization' in Appendix A.

just the exact sequence of events on April 11, 2018. As stated in DOE Standard 3009-94 Change Notice 3, *Preparation Guide for U.S Department of Energy Nonreactor Nuclear Facility Documented Safety Analyses* [5], a hazard analysis "requires evaluation of the complete spectrum of hazards and accidents."³

In fact, the April 2018 event itself demonstrates the importance of taking a broader view after an adverse event. In 2005, in the first year of ARP operations, a drum caught fire when waste was being exhumed from SDA. The investigation into the 2005 event [6] concluded that the most likely cause was the rapid oxidation of uranium, along with the burning of hydrogen released from uranium hydride. The investigation for the 2005 event described the uranium as "roaster oxide," which is depleted uranium that had been put through a roaster at the Rocky Flats site in Colorado. The purpose of the roaster was to oxidize the uranium so it no longer posed a pyrophoric hazard, but the oxidation was incomplete so roaster oxides are still potentially pyrophoric. By contrast, Fluor Idaho's causal analysis report for the 2018 event [1] identifies the oxidation of non-roaster uranium as being the initiator.

Based on interviews, Fluor Idaho's report (p. 28) states that some personnel at RWMC and AMWTP were not aware of pyrophoric hazards posed by materials other than the uranium roaster oxides involved in the 2005 event. As stated in the report,

When asked, what are pyrophoric materials they immediately stated "roaster oxides". They had no knowledge of any other pyrophoric material.

The staff team finds that the 2005 event was a missed opportunity for DOE-ID and its contractors to consider all potential pyrophoric hazards in the waste, not just the specific type of material that was involved in that event. As discussed in Fluor-Idaho's report, another missed opportunity was a 2017 fire at AMWTP involving uranium that was not roaster oxide (pp. xvi, 37, 48). The staff team considers the 2018 event an opportunity to broadly examine the hazards posed by flammable gases and undesired chemical reactions. Similarly, even if beryllium carbide was the main source of methane in the four April 2018 event drums, that does not mean DOE-ID and Fluor Idaho's attention should be limited to beryllium carbide. For example, if certain other types of metal carbides could be in the waste, then those also could hydrolyze and generate flammable gases [7, 8].

The relationship between the 2017 event at AMWTP and the 2018 event at RWMC also demonstrates the importance of fully performing an "extent of condition" review. DOE and its contractors use such reviews to determine whether the discovered problem potentially could exist in other locations. It would be prudent to examine whether other DOE sites could have wastes that generate flammable gases through chemical reactions.

The staff team further notes that chemical reactions in a drum also caused the 2014 radiological release event at WIPP [9]. After that event, DOE took actions to prevent adverse chemical reactions in waste containers, including enhancing the requirements for evaluations of

³ The newest version of the standard, DOE Standard 3009-2014, also includes this concept. This report cites the older version (3009-94 Change Notice 3) because RWMC is applying that version.

chemical compatibility [10]. However, these requirements only had to be met before shipping the waste to WIPP, and so these requirements did not necessarily apply to wastes while they were still at other DOE sites such as INL. Fluor Idaho personnel had not performed the enhanced evaluation for the wastes involved in the April 2018 event.

Methane Flammability—A deflagration involving methane can occur if there is a mixture of methane and an oxidant (such as the oxygen in air) at concentrations that allow a flame to propagate, and an ignition source. The lower flammability limit (LFL) of methane in air, at room temperature, is about 5 percent by volume [11, 12]. In the units used elsewhere in this report, the LFL is about 50,000 parts per million by volume (ppmv). The upper flammability limit (UFL) is about 15-16 percent [11, 12], or 150,000-160,000 ppmv. A deflagration could occur if the methane concentration is between these limits. With waste drums, a measured concentration above the UFL should not be considered to be safe. At some other time or location, the concentration would likely be below the UFL. Finally, the stoichiometric concentration of methane in air is about 9.5 percent by volume. At higher concentrations of methane in a closed system, there is not enough oxygen to support combustion of all the methane.

Methane Limits—DOE anticipates that the waste drum contents will generate flammable gases including hydrogen and methane. DOE assumes the "primary mechanism" for this gas generation is radiolysis [13], which is a different mechanism than Fluor Idaho's hypothesis for the wastes discussed in this report. DOE's approach to preventing deflagrations in waste drums generally involves keeping void spaces in the drum below the LFL. In doing so, DOE considers the combined effect of the various flammable gases and vapors that could be present. DOE's approach is detailed in the requirements [13] (and supporting information [14]) for shipping contact-handled transuranic (TRU) waste in containers known as TRUPACT-II and HalfPACT⁴. TRUPACT-II and HalfPACT are among the containers that DOE uses for shipping waste to WIPP. While DOE's shipping requirements assume that "the predominant flammable gas of concern is hydrogen," they include a limit specifically for methane [13]. When the gas inside the drum is sampled, the methane

concentration must be less than 1,250 ppmv, or else Fluor Idaho cannot ship that drum to WIPP. Personnel from DOE's Central Characterization Program (CCP) conduct the gas sampling at AMWTP.

While DOE-ID is not applying it to waste drums, the National Fire Protection Association (NFPA) has a standard for preventing explosions due to deflagrations [15]. This standard includes a section on preventing deflagrations in an enclosure by limiting the concentration of fuel. The standard states that the enclosure shall be maintained at or below 25 percent of the LFL, with some exceptions that are not relevant to the waste drums. Where methane is the only flammable gas or vapor, this limit is about 12,500 ppmv in air, at room temperature. This value provides additional context for the data presented in the next section.

Filter Vents—For shipments to WIPP, DOE requires that drums must have filter vents installed [10, 13]. Accordingly, when RWMC personnel repackage waste into a new product drum, that drum has a filter vent. These vents "prevent a potential pressure buildup due to

⁴ The shipping requirements are cited here because they affect operations at RWMC and AMWTP. There are additional documents relevant to other types of shipping containers; these are not discussed here for simplicity.

generation of gases by allowing the venting of gaseous products while retaining particulates" [14]. Despite this wording, it should be understood that the vents are intended to allow gases such as hydrogen to diffuse out of the drum; the vents are not designed to prevent lid ejection by relieving pressure in a scenario where pressure is rapidly increasing in the drum.

Discussion. The staff team reviewed the data provided by DOE-ID and Fluor Idaho regarding drums with elevated methane concentrations. As a result, the staff team identified a potential for product drums to have methane concentrations that approach or exceed the LFL, and that DOE-ID would not be aware of these drums. At that point, the staff team evaluated the controls and procedures at RWMC that are relevant to the methane hazard. The staff team's assessment of those controls is divided into three parts:

- DOE-ID's new controls, enacted to help prevent a recurrence of the April 11, 2018, event, may not prevent the packaging of a new product drum with an elevated methane concentration.
- The RWMC safety basis and a DOE standard include unsupported assumptions about the ability of filter vents to keep a drum below the LFL.
- Other controls, already in effect before the April 2018 event, also may be ineffective in preventing or mitigating methane deflagrations in product drums.

Collectively, the staff team found that RWMC lacks effective controls to prevent or mitigate methane deflagrations. These topics are discussed in more detail below.

This paper also includes a discussion of DOE Standard 5506-2007, *Preparation of Safety Basis Documents for Transuranic (TRU) Waste Facilities* [16], as well as the likelihood and consequences of drum deflagrations.

There is some overlap between the conclusions of this report, and Fluor Idaho's causal analysis report. Fluor Idaho's report also highlights the importance of the methane hazard. The Fluor Idaho report discusses a need to "identify and address…process safety actions required associated with methane" as well as a need to evaluate the "existing historical drum population including adequacy of current drum events." However, Fluor Idaho's initial corrective action plan did not specifically address the deflagration hazard discussed in this staff report [17]. DOE-ID subsequently stated that the corrective action plan "does not adequately address all of the conclusions and judgments of need identified in" the causal analysis report, including the judgment of need related to methane hazards [18]. At the time of this staff report, Fluor Idaho has not yet revised its plan to address the comments from DOE-ID.

Potential Safety Item 1—Potential for Unidentified Flammable Drums—Product drums from the SRP and exhumation missions potentially could have concentrations of methane that approach or exceed the LFL, and DOE-ID would not be aware of these drums.

DOE-ID provided the staff team with historical data regarding waste drums with methane concentrations that exceeded the limits for shipments to WIPP (1,250 ppmv). The staff team is aware of 20 such drums that DOE's contractors discovered in 2010-2011. Because these

drums resulted from repackaging wastes exhumed from SDA, they had filter vents. Table 1 shows the highest methane concentrations measured in several of those drums, from data available to the staff team [19].

Drum Identification	Measurement Date	Methane, ppmv	% of methane
Number			LFL ⁵
ARP60106	7/31/2012	169,789	340%
ARP60109	7/31/2012	137,316	275%
ARP60112	8/15/2012	30,763	62%
ARP60115	8/15/2012	20,402	41%
ARP70264	5/2/2012	18,803	38%
ARP60110	8/15/2012	15,241	30%
ARP60111	8/15/2012	4,723	9.4%
ARP60113	8/15/2012	2,677	5.4%
ARP60114	8/15/2012	1,797	3.6%

Table 1. Highest measured methane concentrations in nine drums, from the data available to the staff team. These drums were not involved in the April 2018 event.

Table 1 shows that two drums (ARP60106 and ARP60109) had methane concentrations that well exceeded the LFL of methane in air $(50,000 \text{ ppmv})^6$. While the peak measurement in ARP60106 was also above the UFL, other measurements in that drum (see Table 2) were between the LFL and UFL, indicating the drum would have been flammable if sufficient oxygen were present. The next four drums in had measured concentrations that approached the LFL, and exceeded the NFPA limit. It is possible that higher concentrations could have been observed in these drums, had a measurement been taken at a different time.

Elsewhere within each drum, the concentration of methane could have been even higher than what was measured. The waste is confined inside a vented plastic bag, which is inside the drum. CCP personnel take the gas sample from inside the drum, but outside the bag. DOE's requirements for shipments to WIPP recognize the possibility that flammable gas concentrations inside the bag could be higher than what was measured in the headspace. These requirements include methods for estimating gas or vapor concentrations within the inner layers of confinement [13, 14, 20].

The data above prove that it is possible for vented drums to have methane concentrations that exceed the LFL in air; this should be considered an anticipated condition. In contrast, the documented safety analysis for RWMC assumed that product drums with vents would not attain flammable conditions (discussed further below). Moreover, after Fluor Idaho repackages waste into a product drum, it is possible that a sample for flammable gas analysis will not be taken until months afterwards. CCP personnel perform the flammable gas analysis to meet WIPP shipping requirements, and not to meet any safety requirement for storage or transfer of drums at INL.

⁵ Assumes the LFL of methane is 50,000 ppmv.

⁶ The staff team recently learned of further instances at INL where a vented drum exceeded the LFL, including drums with high concentrations of hydrogen. The staff team is still collecting information about these drums.

Thus there could be drums on-site with flammable mixtures of gases, and site personnel may not be aware of this condition for several months.

Fluor Idaho personnel also stated that there is no requirement for performing flammable gas analysis for drums that will be sent to disposal sites other than WIPP⁷. Further, they said that there are about 700 SRP product drums for which flammable gas analysis has not yet been performed. Some of these drums could have methane concentrations that approach or exceed the LFL. A deflagration could occur if there is some ignition source in a drum that exceeds the LFL. Possible ignition sources are discussed later in this report.

The presence of flammable drums is a hazard. The hazard is exacerbated because DOE-ID and Fluor Idaho would not realize that a drum contained a flammable mixture of gases. If facility personnel know that a certain drum is approaching or exceeding the LFL, they could take additional precautionary or protective measures (although Fluor Idaho does not have any procedures for taking precautions with such drums). Fluor Idaho personnel also stated that they currently have no way to predict which drums are most likely to have higher concentrations of methane (other than actually measuring methane concentrations). Without knowing which specific drums could be approaching the LFL, personnel cannot apply any additional protective measures unless they apply those measures to all drums.

Even for drums where a flammable gas measurement was taken, that measurement may give an incomplete picture of the hazard posed by the drum. Fluor Idaho personnel stated that a single methane measurement below the limit in the shipping requirements was considered sufficient. However, in cases where DOE's contractors took several measurements from the same drum because the drum was over the shipping limit, the changes in methane concentration over time were complex. Over several years, the trend in concentration is downward, but in the short term there can be fluctuations. Table 2 below shows methane concentration increased substantially after the July 3, 2012, measurement. Without the subsequent measurements, the hazard posed by this drum may not have been fully appreciated. Also, even after a long, steady decline in the measured methane concentration, a drum could still pose a hazard. There have been instances where DOE's contractors repackaged the waste in a drum, and the ensuing product drum had a significantly higher methane concentration. This observation suggests that re-arranging or disturbing the waste could renew a methane-generating reaction that had been slowing down.

⁷ Even for drums that DOE ships to WIPP, the shipping requirements include cases where a measurement of flammable gases is not needed for each drum. See Chapter 5 of the CH-TRAMPAC document.

Measurement Date	Methane, ppmv	% of methane LFL ⁸		
(Waste repackaged on June 25 or 26, 2012 into drum ARP60106)				
7/3/2012	36,882	74%		
7/11/2012	116,703	233%		
7/12/2012	106,485	213%		
7/12/2012	115,583	231%		
7/19/2012	140,694	281%		
7/31/2012	169,789	340%		
7/31/2012	140,000	280%		
5/9/2013	15,912	32%		
10/8/2013	19,003	38%		
3/18/2014	6,030	12%		
(Waste repackaged on March 20, 2014, into drum ARP60808)				
5/20/2014	9,756	20%		
1/20/2015	1,448	2.9%		

 Table 2. Methane concentrations in drum ARP60106, measured over time.

Table 1 and Table 2 only show methane data, for simplicity. The drums also contained some hydrogen, although in smaller concentrations. A more complete assessment of flammability would account for the combined effects of all flammable gases and vapors that are present in the headspace.

Of the nine drums shown in Table 1, the methane concentration eventually decreased below the shipping limit in seven drums [19]. The daughters of the other two drums are still above the shipping limit. One drum was recently measured at about 12,000 ppmv of methane, or about 24 percent of the methane LFL.

Potential Safety Item 2—Existing Controls Ineffective for Methane-Generating Waste— After determining that there was a potential for product drums to approach or exceed the LFL, the staff team evaluated the controls that DOE-ID and Fluor Idaho have in place. The staff team found that those controls are ineffective to prevent or mitigate deflagrations in product drums with wastes that generate methane at a significant rate. The discussion of the controls is divided into three parts, below.

2a: New Controls May Not Preclude Methane Drums—After the April 2018 event, Fluor Idaho paused the sludge repackaging and waste exhumation missions. To allow resumption of exhumation activities in ARP-VIII, Fluor Idaho proposed a new control for exhumation work to help prevent a similar event from occurring there [21]. Fluor Idaho documented the new control in an Evaluation of the Safety of the Situation (ESS), and DOE-ID approved the ESS, including the resumption of exhumation in ARP-VIII under the new control [22]. Fluor Idaho and DOE-ID took these actions while Fluor Idaho's investigation of the April 2018 event was still ongoing, including work to identify the source of the methane. The staff team finds that DOE-

⁸ Assumes the LFL of methane is 50,000 ppmv. Some of the repeated measurements in July 2012 were due to DOE contractors testing different methods of measurement, to ensure the results were reliable.

ID's new control may not prevent the packaging of a new product drum that will have an elevated methane concentration, nor was it designed to do so.

Exhumation of waste from the SDA, which Fluor Idaho currently is performing at ARP-VIII, involves several steps. A simplified description of the process is provided here. Using an excavator, an operator removes soil to expose the waste. The operator uses the excavator to remove the waste from its drum or other container, if the waste is still inside such a container. The operator uses the excavator to pick up the waste, and then Fluor Idaho personnel visually examine it using video. If the waste visually resembles the types of wastes that DOE-ID has agreed to remove from SDA ("targeted waste"), then the operator places the waste onto a metal tray. Implementation of the new control begins at this point.

The operator spreads the waste out in the tray, and uses the excavator to "rake" the waste at least twice. Fluor Idaho personnel allow the waste to remain in the tray, exposed to air, for a holding period of at least 24 hours. After the holding period, Fluor Idaho personnel examine a thermal image of the waste in the tray. If they see any sign of an elevated temperature, they repeat the holding period, and examine the thermal image again. Once they see no sign of elevated temperature, Fluor Idaho personnel proceed toward packaging the waste in a new product drum. The new control in the ESS, involving the holding period and thermal monitoring, formally only applies to wastes that include uranium or potentially pyrophoric metals. In practice, Fluor Idaho has been performing these steps with all targeted waste.

The new control is based on the assumption that the exothermic oxidation of uranium initiated the April 2018 event. The intention of the new control is to allow any uranium (or any other pyrophoric metal) to oxidize while it is in the tray, such that it will no longer react and evolve heat once packaged in the drum. The thermal monitoring is intended to detect an ongoing exothermic reaction.

Even though the new control was not specifically designed for the methane hazard, the staff team considered whether this new control would prevent the packaging of new product drums that would have elevated methane concentrations. While the April 2018 event involved the sludge repackaging project and not exhumation of waste, the drums discovered around 2011 with high levels of methane resulted from the exhumation in ARPs. It is thus credible to anticipate that methane generating wastes can be encountered in both missions. Several factors suggest that the new control for exhumation would not reliably prevent the creation of new drums with high methane concentrations.

The first factor is the history of the drums from Table 1. When DOE's contractor at the time realized it had drums with methane levels that exceeded the shipping requirements, the contractor took repeated measurements to see if the methane would subside on its own [19]. When this did not occur for several drums, the contractor opened the drums, and poured the waste onto a tray. The contractor let the waste sit in the tray for several days, exposed to air, while periodically raking it. After letting some waste sit in the tray for about 19 days, the contractor packaged the waste into drum ARP60106 on June 25 or June 26, 2012. The very high methane concentrations in this drum (169,789 ppmv from Table 1) were measured after this point. In the case of drum ARP60109, the waste had been exposed to air in trays for about

50 days before the high measurement shown in Table 1. Thus, the processing history at RWMC shows that letting waste sit, exposed to air in a tray, for at least 24 hours would not preclude the subsequent creation of a drum with high methane levels.

The other part of the new control is thermal monitoring. Fluor Idaho has performed a thermal analysis intended to show that heat released by the oxidation of uranium could be detected using thermal imaging. Fluor Idaho has not performed a similar analysis for the reactions that generate methane. Without an analysis or field data, there is no basis to assume that the methane-generating reactions would necessarily have a detectable thermal signature.

Thus, after considering both aspects of the new ESS control, the staff team finds that this new control would not reliably preclude the creation of new drums that have high methane levels.

2b: Unsupported Assumptions Regarding Filter Vents—The data in Table 1, showing that at least two drums had methane concentrations that exceeded the LFL in air, call into question assumptions that DOE makes about vented drums. DOE is relying on filter vents to provide a function that they may not be capable of providing.

The safety analysis report (SAR)⁹ for RWMC [23] has a scenario that is relevant to product drums with high methane concentrations. That scenario includes flammable gas explosions in repacked vented drums. However, the discussion for this scenario states that "Vents are installed in ARP and SRP product drums to release flammable gases as they are produced, ensuring a noncombustible concentration in the drum." The hazard evaluation allows for the possibility of some accumulation of flammable gases in a product drum, but only in cases where the filter was plugged or the operators inadvertently failed to install the vent. The evaluation further states that a "deflagration in a repackaged vented or unvented drum is considered to be extremely unlikely...."¹⁰

The actual experience at INL shows that the RWMC SAR made an assumption that cannot be supported. As shown in Table 1, there have been ARP product drums where methane accumulated to the flammability limit. These data prove that DOE should not automatically assume that filter vents are capable of keeping a drum below the flammability limits.

A similar assumption can be found in DOE Standard 5506-2007, *Preparation of Safety Basis Documents for Transuranic (TRU) Waste Facilities* [16]. The standard includes a "minimum set of accident events that must be addressed" when the facility has "initiators that could lead to the accident event." While DOE Standard 5506-2007 includes drum deflagration scenarios (Events 6 and 7 in Section 3.3.2), the standard specifies that the deflagration event occurs in a "suspect" container. The standard defines suspect containers as having no vent, plugged vents, or inadequate vents, and then also meeting additional criteria. The standard does not define "inadequate," nor does it suggest any analysis for determining the adequacy of a

⁹ In 10 CFR 830, DOE has requirements for certain categories of facilities to have a documented safety analysis (DSA). For RWMC, this document is called a 'SAR.'

¹⁰ After the April 2018 event, Fluor Idaho and DOE-ID have changed the likelihood of this event from "extremely unlikely" to "anticipated".

properly installed vent in good condition. Again, historical data from INL show that a product drum with a vent can reach the flammability limit. A deflagration in such drums should be considered credible, despite the language in DOE Standard 5506-2007. The Board previously communicated this point in its technical report on deficiencies in DOE Standard 5506-2007 (p. 4-3) [24].

From an engineering perspective, one cannot simply assume that a drum vent will automatically keep the atmosphere inside the drum below the flammability limit. Rather, it is necessary to consider the rate at which flammable gases are generated, and the rate at which those gases can leave the drum. This analysis would have to consider barriers to transport inside the drum, such as bags or other nested containers. If gases such as methane or hydrogen are generated more quickly than they can exit the drum, then those gases will accumulate and the drum may reach a flammable condition.

The staff team found that for shipments to WIPP, DOE does analyze the rate at which gases are generated and the rate at which the gases leave the drum [14]. However, these analytical methods should be carefully evaluated before applying them to defense nuclear facilities with wastes that generate flammable gases through chemical reactions. The shipping requirements do not assume that the principal flammable gas in a drum is methane generated through a chemical reaction. Further, a credible analysis of filter performance may be difficult without reliable information on the rate of that chemical reaction, and how it might change over time.

2c: Other Controls also Ineffective for Methane Deflagrations—Beyond the filter vents and the new control introduced with the recent ESS, the staff team evaluated whether other existing controls would address methane deflagrations. For deflagrations in product drums, the RWMC SAR [23] mentions "provisions to ensure safe handling of any drum found to be bulging, one possible indication of internal pressurization." However, Fluor Idaho personnel stated that the drums in Table 1 with high concentrations of methane were not observed as bulging. Thus, controls related to bulging drums cannot be used to reliably detect and treat drums with high methane concentrations. While the SAR has other controls to mitigate the effects of deflagrations, they are not relevant to product drums and the variety of locations where Fluor Idaho might stage product drums.

The absence of certain possible controls should be noted. Fluor Idaho does not have a procedure for taking additional precautions with drums that are identified as approaching or exceeding the LFL. Section 6 of DOE Standard 5506-2007 includes a list of controls that could be considered for this hazard.

Finally, the product drums might be stored in a location that does not have a confinement ventilation system to limit releases outside the building. There were at least two fortuitous circumstances involved with the April 2018 event. One is that the drum lids were ejected at night, when ARP-V was not occupied. The second is that the drums were still in ARP-V, which has a confinement ventilation system. After drums are packaged, Fluor Idaho often moves them to storage locations (including locations at RWMC and AMWTP) that lack confinement ventilation. If the drum lids had ejected during this movement, or during storage at those other

locations, there likely would have been a spread of radiological material outside the building.

DOE Standard 5506-2007—In March 2018, before the ARP-V event, the Board issued a technical report [24] detailing deficiencies in DOE Standard 5506-2007. DOE contractors that operate facilities with transuranic wastes use the guidance in this standard while preparing the documented safety analyses for those facilities. As discussed in the Board's report (Section 6.B), DOE evaluated the radiological release event at WIPP in 2014 and found that chemical reactions in waste drums can cause releases of greater magnitude than what is described in the standard. While DOE intends to revise the standard, it has not yet done so, nor has it issued complex-wide interim guidance on this matter.

DOE-ID informed the staff team that it has not performed a similar evaluation of the magnitude of the April 2018 event at INL. The April 2018 event also could have implications for DOE Standard 5506-2007, but without performing an evaluation, these implications would not be understood. One observation in this regard was apparent soon after the event. In the INL event, four drums forcefully ejected their lids. DOE Standard 5506-2007 provides a set of accident scenarios to be analyzed in safety analysis, but includes no scenario where four drums can undergo lid loss due to a cause internal to the drums. The standard states that for deflagration events, only two drums need to be considered (pp. 14, 29). In its limited discussion of other over-pressurization events (p. 15), the standard does not state that more than one drum should be considered. Thus, in terms of the number of drums involved, the April 2018 event was not bounded by the assumptions and guidance in DOE Standard 5506-2007. The staff team is continuing to evaluate other aspects of the standard.

Likelihood of Drum Deflagrations—Prior to the April 2018 event, the RWMC SAR considered deflagrations in product drums to be 'extremely unlikely.' After the event, Fluor Idaho and DOE-ID changed this frequency to 'anticipated' [21]. While the staff team agrees that the frequency should be recognized as 'anticipated,' it is not clear why this change was not made in 2012 when the measurements shown in Table 1 were made¹¹. Informed by the data in Table 1, the staff team evaluated the likelihood of an event. The staff team considered the necessary components of a deflagration: sufficient fuel, sufficient oxidant, and an ignition source.

As shown in Table 1, at least two drums had methane concentrations that exceeded the LFL in air. On the grounds that this condition has actually been observed at INL, the possibility of drums exceeding the LFL should be considered anticipated. This is true even if the number of drums exceeding the LFL is an extremely small fraction of the total number of drums processed.

According to DOE Standard 5506-2007, having enough fuel for a deflagration may not be sufficient for an event where the lid is forcefully ejected from the drum. The standard discusses threshold hydrogen concentrations; lid loss may occur above the threshold. The standard does not specify a threshold concentration for methane. The staff team examined published data concerning the pressure rise in an enclosure during hydrogen and methane deflagrations. The maximum pressure rise (typically seen at or near the stoichiometric

¹¹ Fluor Idaho became the contractor in 2016.

concentration) for methane is reported to be similar to that of hydrogen [11, 25, 26]. These data support the conservative assumption that methane deflagrations can lead to lid loss and ejection of waste.

There also must be sufficient oxygen (or other oxidants) for a deflagration to occur. The LFL and UFL values provided in this report are for methane in air. If the oxygen concentration decreases, the flammable range narrows until the point where a deflagration is not possible at any methane concentration [12, 15]. There is the possibility for chemical reactions to consume the oxygen in the drum. Oxygen depletion often has been observed in unvented drums, though it is a slow process [27] and there have been several cases where the drum still had enough oxygen to allow a deflagration [16, 28]. However, the product drums being analyzed here are vented. With a vent, it should be assumed that oxygen is present in the drum headspace. In any case, a lack of oxygen should not be relied upon for safety unless the oxygen concentration is controlled [15].

In the discussion on deflagrations, DOE Standard 5506-2007 states that "Typically in the DOE-complex, the ignition source is assumed to be present." The wisdom of assuming an ignition source is demonstrated by examining the energy required to ignite a deflagration. For methane, published values for the minimum energy required for ignition are around 0.3 millijoules (mJ) [12, 29]. For context of how little energy can be required, one textbook states that the static discharge from a human who walked across a rug has an energy of about 22 mJ [30]. There are several possible ignition sources for the drums. Possibilities include mishandling during movement, chemical reactions inside the drum (including sparks from uranium), and static electricity. While ignition sources should be assumed, it is still prudent to try to limit the available ignition sources, especially when a drum is known or suspected to be approaching the LFL.

Based on this consideration of fuel, oxidant, and ignition source, the staff team finds that there was sufficient information to designate deflagrations in product drums as 'anticipated' in 2012. DOE has a process by which its contractors recognize a potential inadequacy in the safety analysis (PISA), and place the facility in a safe condition [31]. If DOE's contractors at the time had declared a PISA after measuring high methane concentrations in vented drums, they might have identified more effective controls for this hazard.

Consequences of Drum Deflagrations—The RWMC SAR [23] discusses the potential consequences of drum deflagration events. The SAR states that the consequences are low or moderate to the facility worker, low to the co-located worker, and low to the off-site public. Based on these consequences, the SAR did not identify safety structures, systems, and components or specific administrative controls for these hazards.

The staff team is continuing to evaluate the potential consequences of deflagration and over-pressurization events. The staff team is evaluating the assumptions in the SAR, the content of DOE standards, and information related to the April 2018 event.

Conclusions. INL has solid wastes that generate methane through chemical reactions. Methane-generating waste played a role in the April 2018 event where four

drums over-pressurized and ejected their lids, spreading radiological material within the facility. In the past, drums with such wastes have approached or exceeded the flammability limit of methane in air. The staff team finds that RWMC lacks credible controls for the prevention or mitigation of methane deflagrations in drums.

Appendix A: Terminology

This appendix provides clarification on the terms 'over-pressurization,' 'explosion,' and 'deflagration.'

Over-pressurization. Fluor Idaho LLC (Fluor Idaho) and the Department of Energy's (DOE) Idaho Operations Office (DOE-ID) have used terms including 'exothermic event' and 'over-pressurization event' to describe what occurred in Accelerated Retrieval Project (ARP)-V in April 2018. In this context, 'over-pressurization' can be understood to mean that the pressure increased within the drums, to the point that the drum lids were forcefully ejected. To maintain consistency with DOE-ID, the Defense Nuclear Facilities Safety Board's staff also uses the term 'over-pressurization' in this report.

Explosion. As observed by DOE in DOE Handbook 1224-2018, *Hazard and Accident Analysis Handbook*, "explosions can be defined in a variety of ways". Handbook 1224-2018 includes a sample of definitions from different sources. In the April 2018 event, there was a rapid release of high pressure gases from the drums, accompanied by a loud noise. The four drums can be described as having exploded, according to definitions cited in the DOE Handbook. The staff team avoided using this term in this report (except for situations where DOE uses the term) to avoid confusion.

Deflagration. A deflagration is generally defined as a combustion event where the flame front propagates at less than the speed of sound. A deflagration can represent a type of explosion. This staff report analyzes the possibility of a methane deflagration in a drum. The staff team did not evaluate the possibility of a detonation, in which the reaction front propagates at supersonic speeds.

References

[1] Idaho Cleanup Project, *Formal Cause Analysis for the ARP V (WMF-1617) Drum Event at the RWMC*, RPT-1659, 2018.

[2] Coobs, J.H., and W.J. Koshuba, "The Synthesis, Fabrication, and Properties of Beryllium Carbide," *Journal of The Electrochemical Society*, Vol. 99, pp. 115-120, 1952.

[3] Mallett, M.W., E.A. Durbin, M.C. Udy, et al., "Preparation and Examination of Beryllium Carbide," *Journal of The Electrochemical Society*, Vol. 101, pp. 298-305, 1954.

[4] Idaho Cleanup Project Core, *Technical Analysis of Drum Lid Ejections-ARP V*, RPT-1662, 2018.

[5] U.S. Department of Energy, *Preparation Guide for U.S Department of Energy Nonreactor Nuclear Facility Documented Safety Analyses*, DOE-STD-3009-94 CN3, 2006.

[6] Idaho Cleanup Project, *Independent Investigation Report of the November 2005 Drum Fire at the Idaho National Laboratory Site*, 2006.

[7] Bradley, M.J., and L.M. Ferris, "Hydrolysis of Uranium Carbides between 25 and 100°. I. Uranium Monocarbide," *Inorganic Chemistry*, Vol. 1, pp. 683-687, 1962.

[8] Bradley, M.J., and L.M. Ferris, "Hydrolysis of Uranium Carbides between 25 and 100°. II. Uranium Dicarbide, Uranium Metal-Monocarbide Mixtures, and Uranium Monocarbide-Dicarbide Mixtures," *Inorganic Chemistry*, Vol. 3, pp. 189-195, 1964.

[9] U.S. Department of Energy Office of Environmental Management, *Accident Investigation Report Phase 2, Radiological Release Event at the Waste Isolation Pilot Plant, February 14,* 2014, 2015.

[10] U.S. Department of Energy Carlsbad Field Office, *Transuranic Waste Acceptance Criteria for the Waste Isolation Pilot Plant, Rev 8,* DOE/WIPP-02-3122, 2016.

[11] Cashdollar, K.L., I. A. Zlochower, G.M. Green, et al., "Flammability of methane, propane, and hydrogen gases," *Journal of Loss Prevention in the Process Industries*, Vol. 13, pp. 327-340, 2000.

[12] Zabetakis, M.G., *Flammability Characteristics of Combustible Gases and Vapors*, Bureau of Mines Bulletin 627, 1965.

[13] U.S. Department of Energy, CH-TRAMPAC Rev 4, 2013.

[14] U.S. Department of Energy, CH-TRU Payload Appendices Rev 3, 2007.

[15] National Fire Protection Association, *Standard on Explosion Prevention Systems*, NFPA 69, 2014.

[16] U. S. Department of Energy, *Preparation of Safety Basis Documents for Transuranic (TRU) Waste Facilities*, DOE-STD-5506-2007, 2007.

[17] Idaho Cleanup Project, ARP V (WMF-1617) Drum Event Corrective Action Plan, PLN-5710, 2018.

[18] Zimmerman, J.P., "DOE Review of Corrective Action Plan for the Accelerated Retrieval Project V Causal Analysis," Letter to Fluor Idaho LLC, 2018.

[19] Idaho Cleanup Project, *Disposition of ARP Drums with High Headspace Concentrations of Methane*, EDF-10716, 2015.

[20] Liekhus, K.J., S.M. Djordjevic, M. Devarakonda, et al., *Determination of Drum Age Criteria and Prediction Factors Based on Packaging Configurations*, Bechtel BWXT Idaho, LLC for Idaho National Engineering and Environmental Laboratory, INEEL/EXT-2000-1207, 2000.

[21] Idaho Cleanup Project, *Evaluation of the Safety of the Situation for the Drum Event at ARP V (WMF-1617)*, ESS-137, 2018.

[22] U.S. Department of Energy Idaho Operations Office, *Safety Evaluation Report Revision* 4, Addendum C, for ESS-137, Evaluation of the Safety of the Situation for the Drum Event at ARP-V (WMF-1617), 2018.

[23] Idaho Cleanup Project, *Safety Analysis Report for the Radioactive Waste Management Complex - Accelerated Retrieval Project*, SAR-4 Rev 27, 2017.

[24] Defense Nuclear Facilities Safety Board, *Deficiencies in DOE Standard 5506-2007, Preparation of Safety Basis Documents for Transuranic (TRU) Waste Facilities*, DNFSB/TECH-43, 2018.

[25] National Fire Protection Association, *Standard on Explosion Protection by Deflagration Venting*, NFPA 68, 2013.

[26] Salzano, E., F. Cammarota, A. Di Benedetto, et al., "Explosion behavior of hydrogenmethane/air mixtures," *Journal of Loss Prevention in the Process Industries*, Vol. 25, pp. 443-447, 2012.

[27] Ryan, J.P., *Radiogenic Gas Accumulation in TRU Waste Storage Drums*, E. I. du Pont de Nemours and Company, Savannah River Laboratory, DP-1604, 1982.

[28] Conway, J.T., "Defense Nuclear Facilities Safety Board letter to P.M. Golan on safety issues regarding unvented TRU waste drums," December 14, 2004.

[29] Babrauskas, V., *Ignition Handbook*, Fire Science Publishers, 2014.

[30] Crowl, D.A., and J.F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, 2nd ed., Prentice Hall, 2002.

[31] U.S. Department of Energy, 10 CFR Part 830, Nuclear Safety Management, 2001.