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memorandum

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SUBJECT: Hazards Associated with Legacy Nitrate Salt Waste Drums Managed under the Container Isolation Plan

At present, there are 29 drums of nitrate waste salts (oxidizers with potentially acidic liquid bearing RCRA characteristics D001 and D002) that are awaiting processing, specifically to eliminate these characteristics and to allow for ultimate disposition at WIPP. As a result of the Feb. 14th, 2014 drum breach at WIPP, and the subsequent identification of the breached drum as a product of LANL TRU waste disposition on May 15th, 2014, these 29 containers were moved into the Permacon in Dome 231 at TA-54 Area G, as part of the New Mexico Environment Department (NMED) approved container isolation plan. The plan is designed to mitigate hazards associated with the nitrate salt bearing waste stream. The purpose of this document is to articulate the hazards associated with un-remediated nitrate salts while in storage at LANL. These hazards are distinctly different from the Swheat-remediated nitrate salt bearing drums, and this document is intended to support the request to remove the un-remediated drums from management under the container isolation plan. Plans to remediate and/or treat both of these waste types are being developed separately, and are beyond the scope of this document.

Historical Generation of TRU Nitrate Salt Waste

Wastes contaminated with transuranic (TRU) isotopes have been generated at Los Alamos National Laboratory (LANL) since the 1940s in research and development activities for nuclear weapons, nuclear fuel, and related national security missions. Historically, radioactive waste was buried in shallow landfills called Material Disposal Areas (MDAs); Area G at TA-54 first received radioactive waste in 1957 and has served as the primary onsite radioactive waste management facility since 1959.

Nitrate salt wastes result from aqueous nitric acid processing to recover and purify plutonium.¹ After plutonium recovery, the resulting nitric acid solution contains a number of metal ions that result from the processing operations. These nitric acid solutions were concentrated through distillation until the nonvolatile salts in the evaporator were close to saturation. According to procedures, 500 to 600 L of feed was reduced to 10 to 25 L of “bottoms”. The hot evaporator “bottoms” were poured into a water-cooled tray and flash-crystallized, which precipitates primarily nitrate salts and leaves a liquid supernatant. After filtration, the salts were vacuum dried, which consisted of pulling air through the salts using house vacuum for approximately 15 minutes. The nitrate salts from the ion exchange processes were often washed with 3.3 M nitric acid to remove plutonium and ensure they met the Economic Discard Limit (EDL) for plutonium. However, nitrate salts derived from oxalate filtrates were not washed with bulk acid because it would accelerate decomposition of any oxalic acid present in the salts and could result in pressurization of the sealed 55-gallon drums containing the salts with oxalate.

The final composition of nitrate salts depends on the original process feed that was sent to the evaporator. The evaporator feed included ion-exchange effluent (both lean residue and chloride anion) and the filtrate from oxalate precipitation. The majority of LANL MIN02 wastes were derived from the ion exchange feed. Veazey et al documented the composition of the evaporator bottoms from each of these processes for waste batches produced between April 1992 and February 1994.² The solution concentrations³ of the major metal ions from the lean residue are shown in Table 1. Contaminated most often with plutonium and americium, these granular, off-white salts were packaged into plastic bags and placed in containers for temporary, retrievable, onsite storage until a permanent waste facility became available—the Waste Isolation Pilot Plant (WIPP). LANL has used evaporators to concentrate liquids that contain nitrate salts since operations began at the TA-55 Plutonium Processing Facility in 1979.¹ This specific type of TRU waste was generated until 1991, when LANL developed a process to solidify the evaporator bottoms in grout rather than dispose of the nitrate salt waste as granular salts.

¹ (a) Christensen, E. L.; Maraman, W. J. *Plutonium Processing at the Los Alamos Scientific Laboratory*; LA-3542; Los Alamos National Laboratory: Los Alamos, NM, 1969; (b) Christensen, E. L. *Plutonium Recovery at the Los Alamos Scientific Laboratory*; LA-UR-80-1168; Los Alamos National Laboratory: Los Alamos, NM, 1980.

² (a) Veazey, G. W. *TA-55 Evaporator Bottom Characterization*; Los Alamos National Laboratory: 1995. (b) Veazey, G. W.; Castaneda, A. *Characterization of TA-55 Evaporator Bottoms Waste Stream*; NMT-2:FY 96-13; Los Alamos National Laboratory: Los Alamos, NM, 1996.

³ We note that the supernatant fluid metal ion concentrations will not represent the ion concentrations of the precipitated salts, which will be dominated by those metal nitrates with the lowest solubility product.

Table 1. Important metal ion concentrations (median values) in evaporator bottoms from Veazey, et al.² (in g/l)

	Ion Exchange	Oxalate Filtrate
Ca	61	10.5
Mg	58.7	13.3
K	17.6	4.8
Fe	17.0	7.9
Na	7.4	23.9
Al	4.6	2.3
Cr	3.0	1.94
Ni	1.8	1.205
Pb	0.19	0.056

Nitrate salts are oxidizers, with the generally accepted DOT definition that they can promote or initiate combustion in other flammable materials. In general, oxidizers can:⁴

- Intensify combustion
- Widen the flammable range of flammable gases and liquids
- Lower the flashpoints and ignition temperatures of combustible materials so these materials ignite more readily

Typically, the increase in flammability results from either direct reaction of the oxidizer with a combustible material (fuel) or through the release of oxygen, which then stimulates the oxidation or combustion processes.

Thus, the principal hazard of an oxidizer is in its ability to stimulate or promote combustion, which requires fuel. In the case of legacy nitrate salts – those that have not been neutralized and remediated with Spilftyer and Swheat – these legacy salts were processed and stored in a configuration (lead-lined polyethylene liners placed inside of a 55 gallon steel drum) that eliminates this principal hazard. Without the presence of combustible material or fuel, the oxidizers cannot, in storage, lead to combustion. Thus, the un-remediated salts do not present the potential hazard of spontaneous combustion or enhanced combustion in their current configuration, and can be stored in any area in which combustible material is minimized and separated from the nitrate salt bearing containers, without fear of a release of radioactive materials through combustion processes.

⁴ University of Nebraska Lincoln Safe Operating Procedure: Oxidizer Hazards and Risk Minimization

The nitrate salts remediated with Swheat, however, pose just the opposite risk. In this case, the remediation process introduced combustible material (Swheat) to the drum, creating a fuel-oxidizer mixture with the potential for combustion, if heated either internally or externally. In fact, while the specific trigger or ignition of the breached WIPP drum (68660) is still being investigated, there is no question that the fuel oxidizer mixture ignited and burned causing the breach of the drum and releasing radioactive combustion products.

Continued storage of the remediated nitrate salt bearing waste according to the container isolation plan is prudent, to prevent an additional release if one of these drums were to ignite.

DJF:dv

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