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Date: JUN 1 6 2016
Symbol: EPC-DO-16-139
LA-UR: 16-21640
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Mr. John E. Kieling, Chief
Hazardous Waste Bureau
New Mexico Environment Department
2905 Rodeo Park Drive East, Building 1
Santa Fe, NM 87505

Dear Mr. Kieling:

Subject: Transmittal of Finalized Technical Basis Documentation

The purpose of this letter is to transmit a report that the Los Alamos National Security, LLC (LANS) and the U.S. Department of Energy (DOE), the Permittees, committed to providing the New Mexico Environment Department (NMED). As discussed with the NMED staff, the summary included as Enclosure 1 is a justification for the Permittees' decision to not sample unremediated nitrate salt waste. This submittal is a follow-up to Enclosure 3 of the Permittees' *Response to Ordered Action 2/3, Attachment A to Settlement Agreement and Stipulated Final Order HWB-14-20, Los Alamos National Laboratory*. A compact disc that includes the appendices to the document is attached to this submittal.

If you have comments or questions regarding this submittal, please contact Mark P. Haagenstad (LANS) at (505) 665-2014 or Jordan Arnswald (DOE) at (505) 667-6764.

Sincerely,

John P. McCann
Acting Division Leader
Environmental Protection & Compliance Division
Los Alamos National Security, LLC

Sincerely,

Jody M. Pugh
Assistant Manager
National Security Missions
NNSA/Los Alamos Field Office

JPM:JMP:MPH:LRVH/lm

Enclosure: (1) Technical Basis for the Removal of Unremediated Nitrate Salt Sampling (UNS) to Support LANL Treatment Studies

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ENCLOSURE 1

Technical Basis for the Removal of Unremediated Nitrate Salt Sampling (UNS) to Support LANL Treatment Studies

EPC-DO-16-139

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Date: JUN 1 6 2016

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Title:	Technical Basis for the Removal of Unremediated Nitrate Salt Sampling (UNS) to Support LANL Treatment Studies
Author(s):	Funk, David John
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Technical Basis for the Removal of Unremediated Nitrate Salt Sampling (UNS) to Support LANL Treatment Studies

David J. Funk, Deputy Associate Director for Environmental Management
Associate Directorate for Environmental Management
Los Alamos National Laboratory
Los Alamos, NM 87545

Introduction

The sampling of unremediated nitrate salts (UNS) was originally proposed by the U.S. Department of Energy (DOE) and Los Alamos National Security, LLC (LANS) (collectively, the Permittees) as a means to ensure adequate understanding and characterization of the problematic waste stream created when the Permittees remediated these nitrate salts bearing waste with an organic absorbent. The proposal to sample the UNS was driven by a lack of understanding with respect to the radioactive contamination release that occurred within the underground repository at the Waste Isolation Pilot Plant (WIPP) in February 14, 2014, as well as recommendations made by a Peer Review Team. As discussed below, the Permittees believe that current knowledge and understanding of the waste has sufficiently matured such that this additional sampling is not required. Perhaps more importantly, the risk of both chemical and radiological exposure to the workers sampling the UNS drum material is unwarranted. This memo provides the technical justification and rationale for excluding the UNS sampling from the treatment studies.

Discussion

The Remediated Nitrate Salt (RNS) waste is an ignitable,[1] potentially corrosive waste, and must be treated for removal of the characteristic(s) of ignitability and corrosivity prior to off-site shipment for disposal. To better understand the properties of the waste, LANL developed surrogate nitrate salt mixtures by studying the chemical composition of measured salt solutions from Technical Area 55 (TA-55) processing operations,[2,3] and, in one case, studying the process flows for the purification processes, including analyzing the feedstock for chemical constituents using internal process flow diagrams. In addition, the Laboratory sampled the waste from two UNS containers as well as residual waste from five empty parents, which provided insight regarding the aging of these materials.[4,5,6] As an example, all of the observed samples exhibited the presence of lead (Pb) nitrate, which presumably resulted in the interaction of nitric acid with the protective Pb liner of the drum. The analysis utilized software that allows the calculation of the composition of liquid and solid salt fractions using thermodynamic equilibrium principles.[7] These estimates[8] of the solid fractions were utilized to create surrogates of the evaporator bottoms (the solid salts that precipitated during the waste collection phase of the Plutonium purification processes at TA-55). RNS surrogates were formulated through the addition of sWheat Scoop® kitty litter to these salt surrogates and the thermal sensitivity of the RNS surrogates were evaluated using small scale testing that included Differential Scanning Calorimetry (DSC) and Automatic Pressure Tracking Adiabatic Calorimetry (APTAC).[9,10] Testing of these materials demonstrated that the surrogates have low temperature chemical reactions that exhibit exothermic behavior at onset temperatures as low as 42-60 °Celsius (as measured using APTAC).[11] This supports the hypothesis proposed by Clark and Funk,[12] and validated separately by the Technical Assessment Team,[13] that a series of exothermic reactions, starting at room temperature, could lead to thermal runaway that would heat, pressurize, and breach the drum and ultimately, vent radioactive material. We note that thermal runaway results when exothermic chemical heating cannot be offset by cooling from thermal transport (heat removal) out of the drum (conduction/convection/ radiation), leading to increased chemical reaction rate and eventually, runaway.

One question that has been posed by the New Mexico Environment Department (NMED) and the Peer Review Team (PRT) chaired by Dr. Frank Pennebaker, is whether our choice of surrogate is bounding. The original report from the PRT had made the following recommendation:[14]

> "Waste characterization should be the primary focus prior to finalizing a treatability study for remediation and a statistically derived sampling plan on the UNS drums to sufficiently characterize the material for chemical and regulatory components should be developed."

The logic behind this recommendation was driven by the PRT's concern, at that time, that our simulant, which exhibited reactivity at temperatures near 60 °C as measured by APTAC, may not be bounding or representative, and that the mechanism for thermal runaway was still not established adequately to yield confidence in our understanding of the event. The only full-scale test data available for the committee was the initial measurements and video from full-scale drum tests C and D, the heated vented and sealed drums, respectively. As a result of this recommendation, the Permittees prepared a sampling plan to obtain representative samples from the UNS, and to utilize the material in small-scale studies (DSC) for comparison with our surrogates, to confirm that our surrogate is bounding.[15]

Since that time, the full-scale tests have been fully analyzed, and a presentation detailing the results generated.[16] In addition, as noted above, we have continued with our parametric small-scale studies of the Weisbrod-8 (WB-8) simulant, and have found that the thermal sensitivity can be lowered to 42 °C at higher Pb concentrations (4%) and under fuel-lean conditions (15% sWheat).[11] Subsequent to these analyses, the PRT was reconvened in early 2016, to assess our progress and to make additional recommendations in support of our efforts to treat the RNS as expeditiously as possible to eliminate the hazard. As a result of this review, the PRT made two new recommendations that include:[17]

> "Recommendation 1: LANL should document the selection process for surrogates used in testing and provide a concise technical basis for why the surrogate is either conservative (bounding) or representative of the RNS and UNS material for treatment evaluation."
>
> and
>
> "…Previous recommendations suggested sampling of the UNS was primarily focused on better characterization of the waste stream prior to processing RNS. Additionally, in developing the sampling plan, LANL has demonstrated a stronger understanding of the waste stream.
>
> Recommendation 20: LANL should now evaluate whether the sampling is needed for understanding the waste stream."

The change in posture was driven by the full analysis of the test results associated with the full-scale tests, and the fact that the surrogates can exhibit temperatures that would cause reaction in full-scale test starting at room temperature. Our support for this last statement stems from two factors, including:

1) The results from the 25 °C sealed drum-scale test (Drum B) that exhibited a significant temperature rise to nearly 33 °C over a period of several days. While the drum did not fully runaway, a mechanism demonstrating that self-heating could occur at scale with these surrogates, was solidly established.

2) We have conducted extensive modeling of surrogate kinetics using COMSOL (a finite element analysis).[18] Our original intent for these studies was to demonstrate that the likelihood of runaway after 650 days in storage has become exceedingly small (beyond extremely unlikely) when evaluating a drum-scale chemical system with physically plausible chemical kinetics. Within the approximations defined in this model, we believe the statement to be true. In addition, we have utilized this model to evaluate whether a drum consisting of our most sensitive surrogate material (4% Pb, 15% sWheat, with WB-8), using chemical kinetics derived from the test results in (11) would exhibit runaway. At 15 and 25 °C, the drum computationally exhibits thermal runaway in hours (5.6 and 3.3 hours, respectively).

Which brings us to the real question, how do we define bounding? That is to say, what are the characteristics of the material that when adequately understood, lead us to conclude that our surrogate is bounding, and provides confidence that our understanding is adequate, and would eliminate the need for additional characterization. Upon consideration of this question, we have established the following criteria for the definition of a bounding material.

1) The material has sufficient chemical potential (energy content) that would allow for the resulting condition observed within the mine at WIPP. This criterion can be simplified to: contains sufficient concentration of oxidizers as mixed with the fuel to create an ignitable hazard.
2) The material has a rate of reactivity (rate of energy release) that would enable thermal runway as quickly or sooner than the most unstable RNS (drum 68660). That is, the heat generation rate exceeds the heat dissipation rate, accelerating the reactivity, ultimately enabling the pressurization of a container and causing it to breach.
3) The chemical constituents are consistent with the major components expected for the waste form.

For the surrogates we have created, we meet all three criteria as follows.

1) The WB-8 surrogate has been demonstrated to contained sufficient energy to lead to drum pressurization and breach as observed in the full-scale tests.
2) Chemical reactivity as measured in small-scale tests, has been shown (through simulation), to lead to thermal runaway under ambient conditions. We note that this criterion is overly strict for the waste in storage: after 700+ days, no additional drum has experienced thermal runaway, indicating that for the material in storage, the rate of reaction is below the threshold needed to cause thermal runaway. We also note that we observed significant reactivity in the full-scale tests (Drum B), after 12 days, reaching a temperature near 33 °C, arguably near the threshold to achieve spontaneous runaway.
3) The major chemical constituents of the waste are the sWheat and the nitrates themselves, which are what led to the incompatibility. From historical records[4,5,6] and documented summaries, there is no question that the UNS consists of metal nitrate salts, and that we added sWheat kitty litter when processing. Our surrogates are comprised of metal nitrate salts and sWheat kitty litter composition.

Conclusion

As a result of the Permittees testing and analysis, we have demonstrated that our material is bounding, and that our understanding of the drum breach within the mine is adequate.

Thus, to prevent unnecessary exposure to the worker from drum radioactivity, and to eliminate the potential exposure to chemical hazards (e.g., NO_2, nitric acid vapors, etc.) the Permittees do not find a technical need to conduct additional sampling of the UNS in support of our treatment studies, and LANL proposes to move forward without execution of the UNS waste sampling plan.[16]

[1]Ignitability is defined in 40 CFR Part 261 Subpart C, and for the purposes of this discussion is material that "is not a liquid and is capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture or spontaneous chemical changes and, when ignited, burns so vigorously and persistently that it creates a hazard," or can be characterized as an oxidizer.

[2] W. Veazey, A. R. Schake, P. D. Shalek, D. A. Romero, and C. A. Smith, "Waste-Form Development for Conversion to Portland Cement at Los Alamos National Laboratory (LANL) Technical Area 55 (TA-55)," LA-13125 (1996).

[3] G. Veazey, A. Castaneda, Characterization of TA-55 Evaporator Bottoms Waste Stream, Memo NMT-2: FY96-13, October 26, 1996.

[4] P. T. Martinez, R. M. Chamberlin et al., "Analytical Chemistry and Materials Characterization Results for Debris Recovered from Four Nitrate Salt Waste Drums," LA-UR-15-26850 (2015).

[5] P. T. Martinez, R. M. Chamberlin, "Analytical Chemistry and Materials Characterization Results for Debris Recovered from Nitrate Salt Waste Drum S855793," LA-UR-15-27132 Rev. 1 (2015).

[6] L. R. Drake, "Analytical Results from the Area G Nitrate Salt Samples Submitted to C-AAC," LA-UR-14-26900 (2014).

[7] Stream Analyzer® represents many years of work by OLI Systems, to create a tool for predicting the behavior of multi-component aqueous systems. The company worked with national laboratories to create a database that addressed the behavior of Hanford wastes.

[8] K. Weisbrod, K. Veirs, D. J. Funk, and D. L. Clark, "Salt Composition Derived from Veazey Composition by Thermodynamic Modeling and Predicted Composition of Drum Contents." LA-UR-16-21651.

[9] **Differential Scanning Calorimetry (DSC).** DSC measures the thermal response of a material by monitoring the heat flow into or out of that material as it is heated at a constant ramp rate. A 1 mg sample of the material is held in a sealed aluminum pan. The pan is placed in an instrumented furnace with an empty reference pan and the furnace is ramped at 10 ˚C/min while heat flow to the sample and reference pans is monitored. Endothermic events require more heat to flow to the sample to keep its temperature increasing at the desired ramp rate. Exothermic events cause the furnace power to be reduced for the same reason. With this method, melts, phase transitions, decomposition, and other features can be quantitatively measured.

[10] **Automatic Pressure Tracking Adiabatic Calorimetry (APTAC).** APTAC is a measurement that determines the temperature at which a material begins to self-heat and monitors the thermal and pressure behavior of that material during the self-heating. In this test, several grams of material are loaded into a titanium sample bomb that is mounted inside a furnace. The bomb is instrumented with a pressure line and thermocouple that is inserted into the sample. In a typical experiment, the sample is heated in 2 ˚C steps and the temperature is monitored at each step for some tens of minutes. If there is no indication of self-heating, the next step is taken. If the sample does begin to self-heat, the instrument switches to its tracking mode and ramps the furnace at the same rate that the sample is self-heating. This produces adiabatic conditions – the sample cannot lose heat to the surroundings. The heating stops when the heating rate exceeds the limit of the instrument, the pressure exceeds limits, or the sample temperature exceeds a predetermined threshold. The onset temperature of the self-heating is an important metric for ranking materials relative to one another in terms of thermal stability. The adiabatic nature of the measurement makes this more relevant to larger masses whose thermal conductivity may inhibit heat loss from a hot spot. The onset and rate of heating can also be used to determine kinetic parameters that allow predictions to be made for the material in other scenarios, enabling the development of process parameters for reprocessing of the remediated nitrate salt waste stream.

[11] G. Brown, "Remediated Nitrate Salt (RNS) Surrogate Formulation and Testing Standard Procedure," PLAN-TA-9-2443 (U), Rev. B, LA-UR-16-21746, and the associated analytical report, "M7 High Explosives Science and Technology Analytical Laboratory Report Analytical Lab# 52219." LA-UR-16-21770.

[12] D. L. Clark and D. J. Funk, "Chemical Reactivity and Recommended Remediation Strategy for Los Alamos Remediated Nitrate Salt (RNS) Wastes," LA-UR-15-22393, Los Alamos National Laboratory: Los Alamos, NM, February 17, 2015.

[13] Waste Isolation Pilot Plant Technical Assessment Team Report, March 17, 2015, SRNL-RP-20147-01198, Rev. 0.
[14] "LANL Nitrate Salt Remediation Plan Peer Review Summary," SRNL-RP-2015-00420, June 9, 2015.
[15] Sampling and Analysis Plan for Unremediated Nitrate Salt Waste, ENV-DO-15-0248, prepared by L. Vigil-Holtermann, LA-UR-15-26357, Rev. 1 (2015).
[16] D. J. Funk, "The Path to Nitrate Salt Disposition," LA-UR-16-21760 (2016).
[17] Los Alamos National Laboratory Nitrate Salt Waste Remediation Peer Review Team Report, SRNL-MS-2016-00035, February 25, 2016.
[18] E. M. Heatwole, "Evaluation of the Likelihood for Thermal Runaway for Nitrate Salt Containers in Storage at LANL, "LA-UR-16-22002.