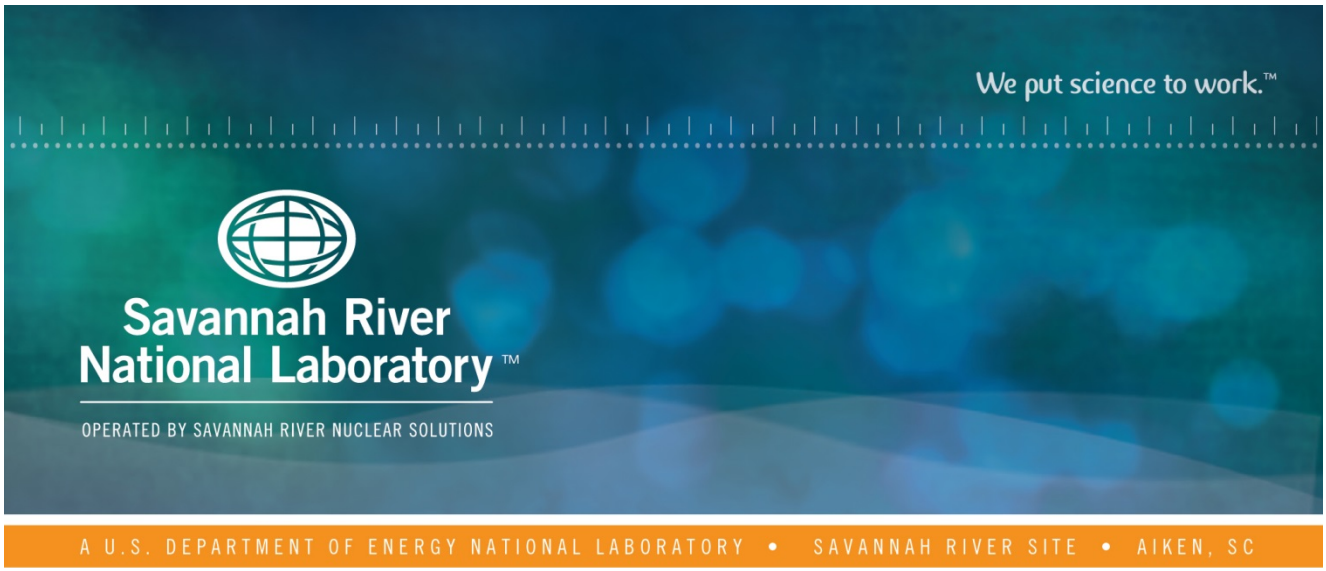

Los Alamos National Laboratory Nitrate Salt Waste Remediation Peer Review Team Report

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Introduction

Savannah River National Laboratory (SRNL) has constituted a team of experts in pertinent scientific and technical disciplines and with operational and assessment experience. The Los Alamos National Laboratory (LANL) Peer Review Team (PRT) members include:

- Dr. Frank E. Pennebaker, SRNL, PRT Lead
- Andrew P. Fellinger, SRNL, PRT Advisor
- Dr. David T. Hobbs, SRNL, Technical Expert
- F. Lee Fox, SRNS, Technical Expert
- Dr. David Rosenberg, SNL, Technical Expert
- Dr. Michael Hobbs, SNL, Technical Expert
- Dr. Michael Kaneshige, SNL, Technical Expert
- Randall Scheele, PNNL, Technical Expert
- Laureen Smith, Bechtel, RCRA Expert
- Tim Burns, LANL Difficult Waste Team, Technical Expert (note: David French filled in for Tim)

Independent Reviewer: Dr. John Marra, Senior Technical Advisor, EM-HQ

The team was requested to review the current plans to treat the remediated nitrate salt (RNS) waste stream and unremediated nitrate salt (UNS) at LANL. In addition to publishing the Options Assessment Report, LANL has developed an Engineering Options Assessment Report, completed the full scale drum tests, conducted an analysis of the likelihood of another drum experiencing thermal runaway using simulation, and began the development of a safety basis strategy for processing. The review team was briefed and advised on the plan and schedule for the remediation of the drums before the start of the next fire season on January 6 and 7, 2016 at LANL. The specific topics covered included:

- Path to Nitrate Salt Disposition
- Options Assessment Report Overview
- Estimated Salt Composition
- Nitrate Salt Processing Schedule
- Full Scale Drum Testing and Implications for Processing
- Evaluation of the Likelihood of Thermal Runaway for Nitrate Salt Containers in Storage at LANL
- RNS Processing Options Engineering Assessment Report and Status of Current Testing
- RNS Surrogate Testing Status
- RCRA Permit: Application, Sampling, Treatment Studies, and Status of Current Testing
- Safety Basis Strategy for Processing RNS Waste

The review was focused on remediation of drums at LANL with a goal of starting within 6-9 months. The PRT was charged with the following specific actions for review at the beginning of the meeting.

1) Provide a technical review of the full scale drum tests and the resulting conclusions.
2) Provide a current assessment of the safety of the drums in storage at LANL
3) Assess the likelihood that operational activities (e.g., drum movement) could initiate thermal runaway.
4) Provide a technical assessment of the treatment options and progress.
5) Provide a technical assessment of the engineering options, including the baseline plan for blending in the Waste Characterization, Reduction, and Repackaging Facility (WCRRF).
6) Evaluate the proposed mitigation strategy (cooling and pressure relief)
7) Evaluate the risks associated with accelerating execution of treatment before the next fire season.

Review

One of the important assumptions in performing the current testing by LANL and Southwest Research Institute (SWRI) is the use of surrogate material to represent the RNS and UNS drums in testing. Current testing has

primarily focused on the use of Weisbrod-8 simulant [1] developed at LANL, but other surrogates have been studied including SFWB11, which exhibits a lower exotherm onset [2]. In the full scale drum test Weisbrod-8 was used along with additional layers of jumbled plastics and liquid nitrate absorbed in Swheat® and mixed with triethanolamine (TEAN). It is LANL's belief that the Weisbrod-8 simulant is sufficiently conservative, "most sensitive" to represent the worst realistic case of materials within the drum [3]. Other simulants have been developed which initiate thermal runaway at lower temperatures; however, LANL believes these simulants are not representative of RNS wastes as they would have experienced thermal runaway reactions in a very short time period after remediation. Additionally, many of the tests have utilized materials that have been treated prior to testing (e.g. size reduction and/or nitration of Swheat®), which increases the reactivity of the mixture as compared to the actual RNS drums. Also, the ratio of fuel to oxidizer in the simulant has varied for different tests along with ratioing by weight and/or volume to determine the most realistic ratio. The PRT assumes that the RNS drums will be processed at a location close to Area G with the most likely location being WCCRF.

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.

1) Full-Scale Drum Testing

The four full scale drum tests were designed to evaluate whether a thermal runaway reaction was feasible for drum 68660, which was identified as the source of the breach at the Waste Isolation Pilot Plant (WIPP) in 2014. The full-scale drum tests provided definitive evidence to the importance of pressure as a contributing factor to reactions with RNS. In particular, Drum C demonstrated that pressure relief could mitigate or quench a runaway condition. Most of the drum testing indicated temperature perturbations in the top layer (nitrate salts mixed with Swheat® layer), however, multiple drums showed signs of thermal activity in the middle layer at a similar time, which represented the liquid nitrate absorbed in Swheat® neutralized with TEAN.

Recommendation 2: LANL testing has primarily focused on surrogates of the nitrate salts. Based on the results from Drum A, LANL should explicitly address lack of TEAN in surrogates for testing.

Recommendation 3: Based on the results showing the effect of venting (or relieving pressure) on a self-sustaining thermal runaway [2], additional venting or pressure relief should be considered during "safeing" of RNS drums prior to processing.

2) Safety of TRU Drums in Storage

All but four of the stored RNS drums have been overpacked in fifty-four Standard Waste Boxes (SWB). These SWBs are currently being monitored for temperature and headspace gas composition on a regular basis. The other four RNS drums (pipe overpacks) are overpacked in 85 gallon drums. LANL has been performing headspace gas monitoring of the SWBs containing the RNS drums. This monitoring has identified the presence of H_2, CO_2, and N_2O in the headspace. Headspace gas monitoring to-date has not indicated the threat of a near-term runaway reaction [4] being correlated to the oxidation gases (CO_2 and NOx concentrations) and temperature. The drums with the highest gas concentration are being monitored more frequently. Note, drums stored at Waste Control Specialists (WCS) in Texas have shown no indication of runaway reaction despite having been exposed to potentially higher temperatures during the summer months than those at LANL. Thus, the PRT believes that the current storage of the drums (using controlled temperatures and gas monitoring) is safe.

Recommendation 4: LANL has provided sufficient evidence that none of the drums are displaying properties of an imminent runaway reaction though there is SWB gas analysis evidence of gas product formation from oxidation. Additionally, LANL modeling has provided evidence that gas monitoring provides enough sensitivity to detect an increase in reaction rate that could lead to thermal runaway. This capability is critical for ensuring safe storage. Visual confirmation would be a convenient method to verify that none of the drums are displaying characteristics (bulging or breaching) due to over pressurization.

Recommendation 5: Borescope examination of the Standard Waste Box interiors is recommended immediately prior to the start of processing for RNS drums to ensure worker safety.

3) Likelihood that Operational Activities could initiate thermal runaway

LANL described a valid concept to maintain safety of the RNS drums prior to processing in the WCRRF glovebox. LANL presented a plan where drums would be cooled to a temperature of ~ 5°C from the current storage condition of ~ 25°C, which is sufficient to slow the chemical reaction rates and minimize loss of water. Recently, Hobbs reported that cooling drums to a temperature of 20°C decreases the chemical reaction rates by a factor of 6 [5]. The PRT has provided additional recommendations for pressure relief and visual examination earlier in this document. With a cooled drum and pressure relief, the drums should be sufficiently safe over the short distance (<5 miles) that drums travel during removal from storage, transportation and opening for processing.

Recommendation 6: LANL should plan to install a freezer/refrigerator for possible drum cooling in WCRRF to eliminate the need to transport drums back to the Permacon if they cannot be processed within 24 hours.

Recommendation 7: LANL should examine the cooling temperature set point of 5°C. It may be more reasonable to select a temperature set point of 20°C if additional venting is in place.

Recommendation 8: In 40CFR 265.173(a), the Environmental Protection Agency (EPA) requires that "a container holding hazardous waste must always be closed during storage, except when it is necessary to add or remove waste." Since the safest approach may be attaching the drum to the glovebox prior to processing, LANL should verify with the New Mexico Environmental Department (NMED) and DOE that a drum attached to the glovebox is considered "closed." This process should be clearly documented in the permit application.

Recommendation 9: LANL should be prepared to demonstrate this to NMED in the mock-up.

4) Technical assessment of the Treatment Options and Progress

LANL has provided a reasonable assessment of treatment options for processing of RNS waste. The PRT believes that the addition of zeolite to the nitrate salt/sorbent mixture in the RNS drums will effectively stabilize and reduce the reactivity of the waste. First, the zeolite will remove any free liquids, which removes the characteristic of corrosivity (D002). Second, addition of sufficient zeolite will produce a mixture that exhibits an endothermic reaction enthalpy rather than an exothermic reaction enthalpy as the mixtures exist today. Thus, it removes the characteristic of ignitability (D001) by rendering the mixture incapable of self-sustained reaction. The zeolite prevents spontaneous chemical changes, which could cause the material to burn so vigorously and persistently that it creates a chemical hazard. Removal of these hazardous characteristics will be demonstrated in the surrogate testing.

However, two assumptions in the initial Options Analysis document have changed since the document has been issued. The first change is warming the drum slightly to facilitate processing rather than the initial plan of keeping them cooled to a safe condition during the addition of zeolite. The second modification is the addition of water as a processing aid for mixing rather than the original plan of mixing the waste with zeolite without the addition of water.

Recommendation 10: The surrogates (including debris) should be tested to verify that the hazardous characteristics have been removed and the resulting waste meets EPA requirements, DOT shipping requirements and the WIPP WAC.

Recommendation 11: Update the Options Analysis document to ensure the document is consistent with the current plans for processing. Additionally, provide the technical basis that the addition of water will not create additional safety problems during the treatment of the RNS.

Recommendation 12: While it is believed that the thermal runaway reactions will be mitigated by zeolite, chemical reactions that produce gaseous products could be occurring after treatment. Additional venting of the drums containing the treated waste (e.g., more than one drum filter vent) should be evaluated.

Recommendation 13: LANL should confirm that the reaction between zeolite and acids in the drum will not cause additional physical (heating), chemical or engineering issues.

Recommendation 14: LANL should perform confirmatory D003 and paint filter testing on surrogate material.

5) Technical assessment of the Engineering Options and Progress

LANL has provided a reasonable argument to process the RNS waste by mixing with zeolite in the WCCRF glovebox. At this point, specific details need to be defined to move forward in a deliberate fashion. It was reported that a Process Flow Diagram has been developed with the specific details of the envisioned process but was not reviewed by the PRT. These details are important in developing the procedures for the treatment process as well as defining the controls for the Safety Basis. The PRT is skeptical that debris rinsing can be achieved with the current plans. Debris is typically at the bottom of the drum; thus, it is anticipated to be processed at the end of the evolution. This rinsing will likely produce a large volume of water. If this water is to be used in the mixing, it can only be processed with the waste from the parent drum (i.e., rinse water cannot be used in mixing of waste from the next drum processed) without creating additional daughter drums.

Recommendation 15: Define how the workers will ensure that the correct ratio of zeolite to waste (weighing, volume, etc.) is added to ensure adequate stabilization. Previous processing appeared to have varying amounts added.

Recommendation 16: LANL should evaluate the current handling of debris to optimize processing.

Recommendation 17: Ensure good log-keeping occurs during processing to validate that appropriate steps were taken to render the material safe and remove the EPA hazardous characteristics.

Recommendation 18: Perform a Time and Motion Study on waste processing to optimize process and minimize dose to the worker.

Recommendation 19: Additional testing performed at LANL should focus on enhancing or refining the processes for remediation.

6) Evaluation of the Proposed Mitigation Strategy

The PRT evaluated the mitigation strategy in the above sections.

7) Risks Associated with Acceleration

Due to a change in the assumptions for the Material at Risk, there is a strong desire to accelerate the schedule. The PRT is concerned that attempts to accelerate the schedule may lead to incomplete or inaccurate technical review and poor documentation.

Additional Considerations

The planning for the remediation has been altered from processing UNS first to processing RNS first to accelerate risk reduction. 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.

The evolution of RNS remediation should be considered a new evolution from a work planning and control perspective which would necessitate thorough review of work packages and training. A mock-up of the WCRRF glovebox would represent an ideal training arrangement.

Recommendation 20: LANL should now evaluate whether the sampling is needed for understanding the waste stream.

Recommendation 21: LANL should include operator training and mock-ups as lead-ins to the first evolution of RNS remediation.

References

1. 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," (Draft, 2015).
2. Parker, G. et al., “The Thermolytic Response of a Surrogate Remediated Nitrate Salt (RNS) Waste Mixture at the Drum Scale,” LA-UR-15-29229, December 2015.
3. “Test Plan for Submittal to the New Mexico Environment Department,” LA-UR-15-27971.
4. Robinson, Bruce A., Christopher P. Parker, “Interpretation of Headspace Gas Observations in Remediated Nitrate Salt Wastes Containers Stored at Los Alamos National Laboratory,” LA-UR-15-22661 (DRAFT), April 2015.
5. Michael L. Hobbs, Memorandum titled “Review of Los Alamos National Laboratory’s (LANL) Remediated Nitrate Salts (RNS),” January 13, 2016.