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Date: JUN 30 2016
Symbol: EPC-DO-16-179
LA-UR: 16-24408
Locates Action No.: Not Applicable

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 Final Summary Report Regarding Nitrate Salt Waste Stream Surrogate Testing

The purpose of this letter is to transmit the final summary 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) in a May 13, 2016 submittal (ADESH-16-076). The enclosed summary report 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. Summary of Remediated and Unremediated Nitrate Salt Surrogate Testing in Support of the Waste Treatment Permit Application to the New Mexico Environment Department (NMED)* is provided as Enclosure 1 and appendices to the report is included on the compact disc included with this submittal. This submittal represents the final report regarding off-site surrogate waste testing conducted to assess treatment effectiveness of zeolite blending stabilization of nitrate salt-bearing waste.

If you have comments or questions regarding this submittal, please contact Mark P. Haagenstad (LANS) at (505) 665-2014 or Karen Armijo (DOE) at (505) 665-7314.

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/ms

Enclosure: (1) Summary of Remediated and Unremediated Nitrate Salt Surrogate Testing in Support of the Waste Treatment Permit Application to the New Mexico Environment Department (NMED)

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ENCLOSURE 1

Summary of Remediated and Unremediated Nitrate Salt Surrogate Testing in Support of the Waste Treatment Permit Application to the New Mexico Environment Department (NMED)

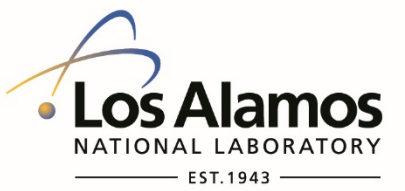
EPC-DO-16-179

LA-UR-16-24408

Date: JUN 3 0 2016

June 2016

Summary of Remediated and Unremediated Nitrate Salt Surrogate Testing in Support of the Waste Treatment Permit Application to the New Mexico Environment Department (NMED)



Prepared by David J. Funk
Deputy Associate Director of Environmental Management

EXECUTIVE SUMMARY

The inadvertent creation of transuranic waste carrying hazardous waste codes D001 and D002 requires the treatment of the material to eliminate the hazardous characteristics and allow its eventual shipment and disposal at the Waste Isolation Pilot Plant (WIPP). This report briefly summarizes the surrogate testing that was done in support of our understanding of this waste form and includes:

1. Small-scale testing that included Automatic Pressure Tracking Adiabatic Calorimetry (APTAC) to evaluate thermal response; impact sensitivity (drop weight impact); friction sensitivity; and sensitivity to electrostatic discharge (ESD).
2. Small-scale testing using Differential Scanning Calorimetry (DSC) coupled with Mass Spectrometry to examine the effect of actinide addition to the thermal sensitivity of the surrogates.
3. Testing demonstrating the effectiveness of two treatment methods proposed to stabilize both the unremediated and remediated nitrate salt waste streams (UNS and RNS, respectively). The two technologies include the addition of zeolite (with and without the addition of water as a processing aid) and cementation.

The testing demonstrates that complex salt mixtures exhibit significant thermal sensitivity, with onset temperatures of as little as 42 °C as measured by APTAC. The surrogates also demonstrate some sensitivity to ESD but are not sensitive to initiation by impact and friction.

Spiking the materials with actinides leads to modest increases in thermal sensitivity and is attributable to reaction chemistry as opposed to radiochemical processes.

Finally, both zeolite addition (with and without water as a processing aid) and cementation were demonstrated as effective remedies for removing the hazardous waste characteristics of ignitability (D001) and corrosivity (D002).

Full reports of the testing of each of theses areas are available and referenced within this summary.

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1.0 BACKGROUND

On February 14, 2014, a radiological release occurred at the U.S. Department of Energy Waste Isolation Pilot Plant (WIPP). A breached nitrate salt waste container originating from Los Alamos National Laboratory (LANL) was later identified as the source of the release.[2] The waste container in question, drum 68660, was improperly remediated and contained an ignitable mixture of nitrate salt waste and organic absorbent material (sWheat Scoop® cat litter).

At the time of generation, the damp salt wastes from plutonium recovery operations were packaged in plastic bags, placed in containers, and put into storage at LANL until a final disposition path was identified. In 2012, the remediation path for the nitrate salt waste was identified to be the addition of kitty litter/zeolite clay to the nitrate salts within the containers and absorption of liquids in the containers also by kitty litter/zeolite clay. These included containers that had previously been remediated using an absorbent called Waste Lock® 770. Therefore, before they are shipped to WIPP, the containers were to be opened in a glovebox, free liquids were to be absorbed with kitty litter/zeolite clay, and the salt material was to be mixed with the absorbent in a ratio that would stabilize the salts. Resulting material was to be repackaged to meet the WIPP waste acceptance requirements. Waste processing of many of these containers was conducted, but the absorbent utilized was an organic kitty litter absorbent instead of the Difficult Waste Team prescription of kitty litter/zeolite clay, resulting in the generation of an incompatible mixture that led to spontaneous combustion of the waste, as documented through investigation into the WIPP event.[1]

From these waste-processing activities, daughter containers were generated that hold the absorbed liquids, nitrate salts mixed with absorbent, and debris from the parent waste container or as generated from the processing of the waste. Containers remaining at LANL include 29 of the original containers, unremediated nitrate salt (UNS) wastes, as well as 60 containers with remediated, absorbed, and repackaged nitrate salt wastes. Containers of remediated and unremediated nitrate salt (RNS) and UNS waste are characterized as exhibiting the U.S. Environmental Protection Agency (EPA) Hazardous Waste Number (HWN) D001 for ignitability (both RNS and UNS waste) and D002 for corrosivity (RNS and UNS waste containers with liquids only). Mixed transuranic waste with D001 and/or D002 EPA HWNs cannot be accepted for disposal at WIPP; therefore, waste treatment of both RNS and UNS waste must be conducted before certification, shipment, and disposal at that facility.

The specific purpose of this report is to summarize the basis for the surrogates that were utilized and to briefly summarize the testing conducted to understand the material thermal and mechanical sensitivities; the effect of actinide addition on the thermal behavior of the surrogates; and the effectiveness of the proposed treatment methods at safely removing the EPA HWNs D001 and D002 from both the UNS and RNS wastes.

2.0 NITRATE SALT SURROGATE DEVELOPMENT

A significant amount of testing was conducted soon after it was identified that a Los Alamos waste container was the source of the radioactive release within the Waste Isolation Pilot Plant (WIPP). This testing has been documented in [1] and captured many of the trials that were conducted to understand the thermal sensitivity and mechanism of the event. To shed light on this mystery and to better understand the properties of the waste, we 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.[4] 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.[5,6,7] 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.[8] These estimates[9] 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). Additional details discussing the choice of surrogate can be found in [10].

The salts were then formulated into mixtures using sWheat Scoop® cat litter and tested to evaluate their sensitivity to thermal and mechanical insult. Nonradioactive surrogates were chosen to allow ease and rapidity of testing whereas the use of radioactive materials would impede the pace of progress in understanding the underlying basis and mechanism for the chemical reactivity that led to the breached drum. As a result if the initial scoping studies, it was determined that at least two factors were critical for ignition of the formulation. These include: 1) the ratio of sWheat Scoop® cat litter to the nitrate salt and 2) the concentration of lead salts in the formulation. The ratio of sWheat to salt influences the oxygen balance of the formulation and therefore the thermodynamic ability to combust without added oxygen, whereas lead nitrate is an apparent catalyst for the ignition process as determined by the scoping studies. The amount of lead actually present in the waste is difficult to estimate precisely due to the complexity of its formation. We also determined that heating and partially drying the materials results in more thermally sensitive materials. To evaluate theses two key parameters and their effect on reactivity, a test plan was constructed to vary these variables and was executed under strict quality control as defined in PLAN-TA9-2443, Rev B.[11]

3.0 SMALL SCALE SENSITIVITY TESTING UNDER PLAN-TA9-2443, REV B

Small scale sensitivity testing is critical to not only demonstrating that the surrogates developed are bounding [10], but to also provide the information needed to establish a basis for controls that will be used to ensure the safety of the worker and public during treatment. Test plan “PLAN-TA9-2443, Rev B” was developed to provide the information needed to establish limits for controls that include temperature (derive a temperature to lower the reactivity, ensuring that thermal runaway is prevented). The initial test plan called for conducting six sensitivity tests that included Differential Scanning Calorimetry (DSC),[12] Drop Weight Impact,[13] Friction,[14] ElectroStatic Discharge (ESD),[15] Vacuum Thermal Stability (VTS),[16] and Automatic Pressure Tracking Calorimetry.[17] However, after the initial round of testing, it was evident that the DSC and VTS were not providing useful data for bounding the drum contents. VTS is intended to evaluate the stability of compounds relative to gas generation as they are heated: we had previously noted that these material off-gas and as a result, this testing was not providing new information (in fact, we identified that gas generation and subsequent pressurization is key to creating the conditions that lead to thermal runaway). In addition, we found that the DSC data was essentially providing similar information as the APTAC, with less fidelity and greater fluctuations, primarily due to the small quantities used in the test. As a result, sensitivity testing was restricted to Impact, Friction, ESD, and APTAC for all remaining rounds of the study.

Shown below is the test matrix that was developed to examine effect of salt to sWheat ratio as well as the effect of lead on the onset temperature of self-heating. All tests were conducted in triplicate to ensure the absence of anomalous results.

Table 1. RNS Surrogate Formulation Matrix.

(weight percent values shown)

	Increasing sWheat ->		
Increasing Lead ->	4% $Pb(NO_3)_2$ 15% sWheat 81% WB-8	4% $Pb(NO_3)_2$ 25% sWheat 71% WB-8	4% $Pb(NO_3)_2$ 35% sWheat 61% WB-8
	2% $Pb(NO_3)_2$ 15% sWheat 83% WB-8	2% $Pb(NO_3)_2$ 25% sWheat 73% WB-8	2% $Pb(NO_3)_2$ 35% sWheat 63% WB-8
	1% $Pb(NO_3)_2$ 15% sWheat 84% WB-8	1% $Pb(NO_3)_2$ 25% sWheat 74% WB-8	1% $Pb(NO_3)_2$ 35% sWheat 64% WB-8

3.1 Summary of Sensitivity Testing

Test results are documented in [18]. Sensitivity testing showed all formulations were insensitive to impact and friction although most had some sensitivity to spark discharge (confirming the need for non-sparking tools when processing these materials). Shown in Table 2 is a comparison of APTAC data from all three rounds of testing showed no obvious trends with sWheat or Pb content with the exception that the 15% sWheat formulations exhibited self-heating onset temperatures that were about 5 °C lower than those of the other formulations. Onset temperatures for all mixtures in the second round of testing ranged from 42 °C to 64 °C, with an average of 54 °C. It is interesting to note that the formulations with the greatest oxidizer concentration led to the lowest onset temperature, with implications as to how the mechanism by which a drum of material could thermally runaway (inadequate mixing; not meeting the expected 3:1 sWheat to salt ratio).

Table 2. Temperatures of Onset of Self-heating

Each cell contains onset temperatures from all three rounds of testing (rounds 1 to 3 ordered from top to bottom in each cell).

	15 % sWheat	**25 % sWheat**	**35 % sWheat**
4% Pb	42 ˚C 48 ˚C 50 ˚C	56 ˚C 56 ˚C 58 ˚C	64 ˚C 58 ˚C 56 ˚C
2 % Pb	48 ˚C 48 ˚C 44 ˚C	56 ˚C 56 ˚C 60 ˚C	60 ˚C 52 ˚C 58 ˚C
1% Pb	52 ˚C 48 ˚C 50 ˚C	52 ˚C 59 ˚C 54 ˚C	58 ˚C 54 ˚C 56 ˚C

Finally, shown in Table 3 is the set of kinetic parameters derived from the APTAC data. The data were fit to first-order Arrhenius kinetics using software that accompanies the instrument. These parameters are then used to establish the effect of temperature.

Table 3. Arrhenius Kinetic Parameters

Established for the initial self-heating segments of the RNS surrogate formulations. "A" is the pre-exponential factor in log(1/s) and "Ea" is the activation energy in kJ/mol. Each cell contains kinetic parameters from all three rounds of testing (rounds 1 to 3 ordered from top to bottom in each cell).

SFWB8-15-4	SFWB8-25-4	SFWB8-35-4
A = 4.5, E_a = 63	A = 5.4, E_a = 62	A = 8.3, E_a = 85
A = 11.1, E_a = 106	A = 9.7, E_a = 95	A = 6.4, E_a = 73
A = 7.1, E_a = 77	A = 7.3, E_a = 77	A = 8.2, E_a = 86
SFWB8-15-2	SFWB8-25-2	SFWB8-35-2
A = 9.4, E_a = 93	A = 12.1, E_a = 116	A = 8.5, E_a = 88
A = 6.4, E_a = 71	A = 11.8, E_a = 103	A = 8.1, E_a = 80
A = 7.9, E_a = 84	A = 7.3, E_a = 77	A = 7.7, E_a = 83
SFWB8-15-1	SFWB8-25-1	SFWB8-35-1
A = 11.9, E_a = 113	A = 11.2, E_a = 110	A = 11.0, E_a = 107
A = 9.7, E_a = 95	A = 9.9, E_a = 97	A = 12.6, E_a = 118
A = 9.5, E_a = 94	A = 7.7, E_a = 81	A = 7.8, E_a = 82

By calculating the effect that temperature has on reaction rate, we can derive a control that decreases the likelihood of reaction occurring during processing, as follows:

> Thermal runaway and drum pressurization will occur when the rate of chemical reaction (heat and gas production) exceeds the capacity of the container to dissipate the heat and gas generated. Conceptually, this can be described using the following two expressions:
>
> (1) $Q_{eff} = Q_{gen}/Q_{diss}$; where Q_{gen} is the heat generation rate and Q_{diss} is the heat dissipation rate
> (2) $G_{eff} = G_{gen}/G_{diss}$; where G_{gen} is the gas generation rate and G_{diss} is the gas dissipation rate

Thus, runaway and drum breach will occur when both Q_{eff} and G_{eff} exceed "one", that is, when the heat and gas production rate exceeds the dissipation capacity of the waste container, increasing temperature and pressure until the drum breaches. We note that the gas generation rate is directly correlated with the heat generation rate. Therefore, reducing the heat generation rate will lead to a reduced gas production rate. By cooling the waste, we can lower both the heat and gas generation rates, providing margin against thermal runaway, protecting the worker and public, during transport and while in storage.

4.0 EFFECT OF ACTINIDES ON THE THERMAL SENSITIVITY OF RNS SURROGATES

Prior to conducting much of the small-scale sensitivity work and to establish that our nonradioactive surrogates effectively bounded sensitivity, we proposed a study to evaluate the role that actinides might play in enhancing the reactivity of nitrate salt/sWheat mixtures. The work is documented in the associated test plan and summary report.[19,20]

4.1 Summary of the effect of actinides on RNS surrogate thermal sensitivity

To evaluate the effect of actinide addition on RNS surrogates, Simultaneous Thermal Analysis (STA) was utilized. STA combines traditional thermogravimetric analysis (TGA – the monitoring of mass changes over a controlled temperature profile) with differential scanning calorimetry (DSC – the monitoring of heat flow into and out of the reacting sample over the same temperature profile). Gases generated by the STA are analyzed using quadrupole mass spectrometry (MS).

The effect of actinides was evaluated using comparative methods by monitoring changes in heat activity and product generation. 1.0 to 1.5 g surrogate samples of nonradioactive RNS were analyzed, a second set was analyzed with 100-200 µL 10M HNO3 + 0.3 M HF added, and a third set was analyzed after 200 µL of a concentrated Pu-Am spike (in 10M HNO_3 + 0.3 M HF) was added. The acid and spike solutions were formulated using reagent-grade HNO_3 and HF, which was also used to dissolve a small quantity of mixed, high-fired PuO_2 / AmO_2 oxide. The test matrix is shown in Table 4 and was executed in triplicate.

The thermal behavior of all surrogate samples—unspiked and spiked—is dominated by three basic phenomena: 1) an endothermic dehydration reaction which onsets between ~38 and 50 °C, 2) an exothermic reaction which onsets between 108 and 123 °C related to the rapid gas release, foaming and expansion of the sample, and 3) steady-state, and slightly exothermic, combustion of the foamed sample above ~150 °C. Stage 1 is dominated by the release of copious amounts of H_2O and mass losses between 35 and 45%. Stage 2 is marked by a sudden increase in the NO_x and CO_2 content of the offgas as H_2O begins to tail off. The sustained release of small amounts of CO_2 and lesser amounts of NO_x and H_2O is typical of Stage 3.

The thermal behavior of the RNS surrogates is remarkably consistent and repeatable, given their generally inhomogeneous nature. Varying amounts of lead nitrate in the RNS surrogates has only a slight—if any—effect on the observed thermal behavior. The surrogates containing 1% and 2% $Pb(NO_3)_2$ appeared to be slightly more reactive between ~70 and 115 °C than the formulation containing 4% $Pb(NO_3)_2$. Some of the 1% and 2% samples showed small exotherms near or at the base of the dehydration endotherm. Both the onset and cessation of foaming occur at similar temperatures and the mass losses during dehydration / foaming is also similar for all Pb concentrations.

The thermal behavior and offgas content of the as-received and acid-doped RNS surrogates are broadly similar. While several of the 1% and 2% $Pb(NO_3)_2$ samples exhibited small exotherms in the ~80 and 110°C region, this behavior was neither consistent nor predictable. In most cases, these small exotherms were accompanied by near-vertical spikes in the NO_x content of the offgas. The addition of the acid (and the Pu-Am spike) increased the slope of the foaming reaction.

When spiked with the Pu-Am solution, every surrogate sample showed increased exothermic activity and multiple, transient, near-vertical NO_x offgas maxima in the region between ~80 and 115 °C. In the Pu-Am spiked samples, these exotherms have a characteristically jagged, multi-peaked appearance, and are similar to the corresponding multiple NO_x peaks. The addition of an extra 100 µL of Pu-Am spike to one sample (300 µL of Pu-Am spike, total) did not increase the reactivity of the surrogate relative to the other Pu-Am-spiked runs.

In summary, the STA-MS testing of RNS surrogate indicates that the addition of 3.12 mg Am and 5.54 mg Pu (as 200 μL of a Pu - Am solution in 10M HNO_3 / 0.3M HF) to 1.0 to 1.5 g samples of three RNS surrogate formulations increases reactivity in the 75-115 °C region in each, relative to that of the surrogate alone. Spiking the RNS surrogate with a similar volume of the same HNO_3-HF acid solution with no SNM content changed its thermal behavior only incrementally, by comparison. We further speculate that the observed phenomena are related to the chemical reactivity of the actinide compounds, and are not related to their radioactivity.

These results support the hypothesized mechanism that led to the breach of 68660: low-temperature chemical reactions leading to gas generation and pressurization (increased gas rates are shown here with actinide addition) yield conditions that increase the heat generation rate, further increasing reactivity and gas generation leading to thermal runaway. However, as discussed in [10] actinides are not required for generation of surrogates that lead to runaway, though from these tests indicate that the addition of actinides could lead to more rapid runaway than surrogate waste created from nonradioactive materials alone.

Table 4. Actinide RNS Test Matrix

1% $Pb(NO_3)_2$ 15% Swheat 84% WB-8	2% $Pb(NO_3)_2$ 15% Swheat 83% WB-8	4% $Pb(NO_3)_2$ 15% Swheat 81% WB-8
1% $Pb(NO_3)_2$ 15% Swheat 84% WB-8 100-200 μL 10M HNO_3 + 0.3 M HF	2% $Pb(NO_3)_2$ 15% Swheat 83% WB-8 100-200 μL 10M HNO_3 + 0.3 M HF	4% $Pb(NO_3)_2$ 15% Swheat 81% WB-8 100-200 μL 10M HNO_3 + 0.3 M HF
1% $Pb(NO_3)_2$ 15% Swheat 84% WB-8 200 μL Pu, Am in 10M HNO_3 + 0.3 M HF	2% $Pb(NO_3)_2$ 15% Swheat 83% WB-8 200 μL Pu, Am in 10M HNO_3 + 0.3 M HF	4% $Pb(NO_3)_2$ 15% Swheat 81% WB-8 200 μL Pu, Am in 10M HNO_3 + 0.3 M HF

5.0 TESTING TO EVALUATE THE EFFICACY OF PROPOSED TREATMENT OPTIONS

Two stabilization treatment methods were examined for their effectiveness in the treatment of both the UNS and RNS wastes using surrogates and include (1) the addition of zeolite (with and without the addition of water) and (2) cementation as identified as preferred treatment options in [21]. While both processes are demonstrated to be effective,[22] addition of zeolite has been selected as the preferred method, based on the results of several previous studies and analyses that specifically examined the

effectiveness of this process for deactivating nitrate salts.[23] Cementation was also assessed because of the prevalence of cementation as an immobilization method for similar wastes at numerous facilities around the DOE complex, including at LANL. However, in discussions with transuranic waste experts around the complex, we found that cementation is not a desirable means of treatment because of potential problems associated with dewatering and potential void generation within the material. Given the results we derived with zeolite, this option will not be pursued further.

5.1 Testing Methodologies

LANL's hazardous waste permit specifies testing methodologies to support characterization of hazardous wastes and include the following methods (additional details can be found in [22]):

SW-846 Test Method 1030

SW-846 Test Method 1030 is used to help identify those solids that are "capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture or spontaneous chemical changes and, when ignited, burn[s] so vigorously and persistently that it creates a hazard" [40 Code of Federal Regulations 261.21(a) (2)]. It is appropriate for pastes, granular material, solids that can be cut into strips, and powdery substances.

SW-846 Test Method 1050

SW-846 Test Method 1050 provides a test procedure that may be used to evaluate and categorize liquid and solid wastes that are likely to spontaneously combust.

UN O.1 Test: Test for Oxidizing Solids

UN O.1 is designed to measure the potential for a substance to increase the burning rate or burning intensity of a combustible substance when the two are thoroughly mixed. Tests are conducted on the substance to be evaluated mixed with dry fibrous cellulose in mixing ratios of 1:1 and 4:1 by mass of sample to cellulose. The burning characteristics of the mixtures are compared with the standard 3:7 mixture by mass of potassium bromate to cellulose. If the burning time is equal to or less than the standard mixture, the burning times are compared with those from the Packing Group I or II reference standards.

UN O.2 Test: Test for Oxidizing Liquids

UN O.2 is designed to measure the potential for a liquid substance to increase the burning rate or burning intensity of a combustible substance when the two are thoroughly mixed or to form a mixture that spontaneously ignites. The liquid is mixed in a 1:1 ratio by mass with fibrous cellulose and heated in a pressure vessel while the rate of pressure rise is determined.

Test Method 9095B (Paint Filter)

Test Method 9095B is used to determine the presence of free liquids in a representative sample of waste.

These methods were utilized to demonstrate that 1) the baseline surrogates exhibit the hazardous characteristic of ignitability and 2) the proposed treatment methods remove the hazardous characteristic.

5.2 Testing Overview

Southwest Research Institute (SwRI), a certified EPA laboratory, was contracted to provide qualified personnel, equipment, materials, and facilities to formulate and analyze waste surrogates and treatment options in support of LANL's effort to evaluate RNS waste and to provide insight into the effectiveness of treatment options. This effort included formulating surrogate nitrate salts, preparing nitrate salt solutions, and blending the nitrated salts or solutions with sWheat Scoop® cat litter, zeolite, cement, water, or Waste Lock® 770. The effectiveness for cementation as a treatment technology and the addition of zeolite were assessed for surrogate nitrate salt wastes and the blends prepared to simulate treatment to ensure that RCRA characteristics of ignitability (and corrosivity, where applicable) are removed from the waste after treatment. Debris waste found in the drums was also submitted for evaluation and examination of the impact of RNS waste and UNS solution on the behavior of the debris when it undergoes reactivity testing.

5.3 Testing results

Details of the testing can be found in [22]. A brief summary and discussion is provided here.

5.3.1 Surrogate RNS Waste Blends to Simulate RNS Waste

As identified in Table 5, neat nitrate salts are good oxidizers (Blends 1 and 5), and when mixed with sWheat in ratios of 1:1 or greater, exhibit the characteristic of ignitability (WB8 fails the 1050 test and KNO_3 fails the UN O.1 test). It is interesting to note that at higher concentrations of sWheat, the material would not be considered ignitable based on these tests. Because it is not clear what concentration of sWheat was used in the remediation process, the use of sWheat with nitrates supports application of HWN D001 to this waste form. However, estimates of sWheat to salt ratio in drum 68660 were found to be closer to 1:1, consistent with the most reactive materials identified here.[18]

Table 5
RNS Surrogate Waste & Test Results

	Blend Compositions			Test Results		
	KNO_3 (g)	WB8 Salt (g)	Salt:sWheat Volume Ratio	SW-846 Test Method 1030	SW-846 Test Method 1050	UN O.1 Testing
Blend 1	50	0	1:0	NA*	NA	Packing Group II
Blend 2	50	0	1:1	Nonflammable	Not self-heating	Packing Group III
Blend 3	50	0	1:3	Nonflammable	Not self-heating	Not Div. 5.1
Blend 4	50	0	1:4	Nonflammable	Not self-heating	Not Div. 5.1
Blend 5	0	50	1:0	NA	NA	Packing Group III
Blend 6	0	50	1:1	Nonflammable	Packing Group III	Not Div. 5.1
Blend 7	0	50	1:3	Nonflammable	Not self-heating	Not Div. 5.1
Blend 8	0	50	1:4	Nonflammable	Not self-heating	Not Div. 5.1
Blend 25	0	50	1:0.5	Nonflammable	Packing Group III	Packing Group II

*NA = Not applicable.

5.3.2 RNS Surrogate Blends treated with Zeolite

Blending waste surrogates with zeolite was assessed for effectiveness to remove the D001, ignitable, designation from the RNS waste.

The RNS surrogate wastes prepared for testing and presented in Table 6 were mixed with zeolite and evaluated to understand the effect on ignitability, spontaneous combustion, and oxidizer testing. Recipes tested for zeolite blending with the surrogate RNS waste include volume ratios of 1:0, 1:1, 1:3, and 1:4 RNS waste to zeolite. KMI Zeolite, 100% Multipurpose Zeolite (14 × 40 mesh), was used in the testing. Zeolite was manually mixed with the waste surrogate mixtures. The blends were then allowed to set for 24 h before evaluation tests were performed.

The addition of water before the addition of zeolite is expected to be beneficial to the blending process as well as to reduce the amount of salt (oxidizer) available for the organic sWheat. The intent is to blend the salt/sWheat mixture with water before it is blended with zeolite.

As noted in Table 6, the addition of zeolite in ratios of 2:1 or greater was effective at eliminating the characteristics of ignitability and corrosivity (no liquids). The process was also effective for all blends involving the addition of zeolite using water as a processing aid (our preferred approach as established in 24), demonstrating the robustness of this approach. Note that Blends 9 and 10 represent solid component for UNS, and Blends 11 through 24 represent solid component for RNS blends. This is not surprising given the test results identified in [23], in which zeolite was effective at eliminating the oxidizing potential of nitrates at ratios as low as 1.2:1. Thus, stabilization using zeolite is effective at eliminating D001 and D002 from salt/sWheat mixtures.

Table 6
Blending Recipes for RNS Surrogates

	RNS Surrogate Waste Composition			Zeolite Blend Recipe (S/S = salt/sWheat)		Test Results			
Blend #	KNO3 (g)	WB8 Salt (g)	Salt:sWheat Volume Ratio	Water:(S/S) Volume Ratio	Zeolite:(S/S) Volume Ratio	SW-846 Test Method 1030	SW-846 Test Method 1050	UN O.1 Testing	Paint Filter Test Method 9095B
Blend 9	50	0	1:0	NA	3:1	NA: Salt	NA: Salt	Not Division 5.1	No water added
Blend 10	0	50	1:0	NA	3:1	NA: Salt	NA: Salt	Not Division 5.1	No water added
Blend 11	0	50	1:1	NA	3:1	Nonflammable	Not self-heating	Not Division 5.1	No water added
Blend 12	0	50	1:3	NA	3:1	Nonflammable	Not self-heating	Not Division 5.1	No water added
Blend 13	0	50	1:4	NA	3:1	Nonflammable	Not self-heating	Not Division 5.1	No water added
Blend 14	0	50	1:1	1:1	3:1	Nonflammable	Not self-heating	Not Division 5.1	No free liquids
Blend 15	0	50	1:3	1:1	3:1	Nonflammable	Not self-heating	Not Division 5.1	No free liquids
Blend 16	0	50	1:4	1:1	3:1	Nonflammable	Not self-heating	Not Division 5.1	No free liquids
Blend 17	0	50	1:1	1:1	2:1	Nonflammable	Not self-heating	Not Division 5.1	No free liquids
Blend 18	0	50	1:3	1:1	2:1	Nonflammable	Not self-heating	Not Division 5.1	No free liquids
Blend 19	0	50	1:4	1:1	2:1	Nonflammable	Not self-heating	Not Division 5.1	No free liquids
Blend 20	0	50	1:1	0.5:1	2:1	Nonflammable	Not self-heating	Not Division 5.1	No free liquids
Blend 21	0	50	1:3	0.5:1	2:1	Nonflammable	Not self-heating	Not Division 5.1	No free liquids
Blend 22	0	50	1:4	0.5:1	2:1	Nonflammable	Not self-heating	Not Division 5.1	No free liquids
Blend 23	0	50	1:0.5	0.5:1	3:1	Nonflammable	Not self-heating	Not Division 5.1	No free liquids
Blend 24	0	50	1:0.5	0.5:1	2:1	Nonflammable	Not self-heating	Not Division 5.1	No free liquids

5.3.3 Cementation of RNS Surrogate Blends

Cementation (Cmnt) was the other primary treatment option identified and recommended in the Options Assessment Report[21] and reviewed for implementation at LANL in the Engineering Options Assessment Report.[25] Testing of cementation recipes at the bench scale at LANL were evaluated at SwRI.

A total of 10 cementation tests were conducted. Surrogate blends for cementing the surrogate waste with Type I/II Portland cement are shown in Table 7. All the formulations with sWheat maintain a 4:1 water-to-sWheat mass ratio. Testing at LANL previously used a 3.5:1 water-to-sWheat mass ratio. A higher ratio was used to reduce the amount of RNS waste in the cemented product and to ensure better remediation performance. The water-to-cement mass ratio for the tests ranged from 0.5:1 to 0.75:1. The lower ratio should provide a stronger, drier material. Additional details can be found in [22].

The results of stabilization with cement are also found in Table 7. In all cases, stabilization was demonstrated to remove the D001 characteristic for this material. In discussions with transuranic waste experts around the complex, we found that cementation is not a desirable means of treatment because of potential problems associated with dewatering and potential void generation within the material and was not pursued further.

Table 7
Cement Recipes and Reactivity Test Results for Cementation Tests

	RNS Surrogate Waste Composition [a]				Cement Formulation			Test Results		
Cement Mix Number	KNO3 (g)	WB8 (g)	sWheat (g)	Salt:sWheat Ratio [b]	Water (g)	Cement (g)	Water: Cement Ratio [b]	SW-846 Test Method 1030	SW-846 Test Method 1050	UN O.1 Testing
Cmnt 6	130	0	0	NA[c]	373	495	0.75:1	Nonflammable	Not Self Heating	Not Div 5.1
Cmnt 7	0	130	0	NA	373	495	0.75:1	Nonflammable	Not Self Heating	Not Div 5.1
Cmnt 8	0	225	75	3:1	300	400	0.75:1	Nonflammable	Not Self Heating	Not Div 5.1
Cmnt 9	0	88	88	1:1	352	470	0.75:1	Nonflammable	Not Self Heating	Not Div 5.1
Cmnt 10	0	68	91	0.75:1	364	485	0.75:1	Nonflammable	Not Self Heating	Not Div 5.1
Cmnt 11	0	82	82	1:1	328	504	0.65:1	Nonflammable	Not Self Heating	Not Div 5.1
Cmnt 12	0	72	72	1:1	288	576	0.5:1	Nonflammable	Not Self Heating	Not Div 5.1
Cmnt 13	0	212	70	3:1	282	432	0.65:1	Nonflammable	Not Self Heating	Not Div 5.1
Cmnt 14	0	63	84	0.75:1	336	517	0.65:1	Nonflammable	Not Self Heating	Not Div 5.1
Cmnt15	0	80	80	1:1	320	530	0.60:1	Nonflammable	Not Self Heating	Not Div 5.1

[a] Water-to-sWheat mass ratio = 4:1 for all test mixes.

[b] Mass ratio.

[c] NA = Not applicable.

5.3.4 UNS Surrogate Solution Blended with sWheat Scoop® Cat Litter (including those neutralized with Kolorsafe®)

Blending UNS Surrogate Solution with zeolite was assessed for effectiveness. UNS Surrogate Solution represents the solution found in UNS drums. This surrogate solution simulates the free liquid found in the UNS drums and absorbed into sWheat kitty litter during the preparation of the current set of RNS drums located at LANL. The blends described in this section represent material found in both RNS drums. We note that the identified UNS solution did not exhibit the characteristic of ignitability as the pure liquid, but only upon addition with sWheat. As a result, we prepared additional surrogates that are liquid oxidizers, to ensure that our remedy is bounding. These additional tests are discussed in Section 5.3.6.

Because processing at WCRRF often involved neutralizing liquids using Spilfyter® Kolorsafe®, some of the blend recipes require the addition of Spilfyter® Kolorsafe® to neutralize the pH of the UNS surrogate solution before it is mixed with sWheat to create a representative surrogate. For these formulations, Spilfyter® Kolorsafe® liquid acid neutralizer addition is added to achieve an apparent pH ~of 4 to 9 as measured with Hydrion® pH paper.

In addition to the RNS waste processed with sWheat, four containers were processed with Waste Lock® 770 to absorb the free liquids from UNS parent containers. We have included testing using Waste Lock® 770 to establish the effectiveness of adding zeolite for these materials to eliminate the characteristics of ignitability and corrosivity.

As Table 8 indicates, most of the liquid surrogate/sWheat mixtures exhibited the characteristic of ignitability through failure of the 1050 tests. Addition of zeolite and use of water as a processing aid demonstrated the elimination of both the ignitability (D001) and corrosivity (D002) characteristics for the surrogate liquid and demonstrated the effectiveness of this stabilization method for these waste forms.

Table 8
UNS Surrogate Solution Blend Recipes and Test Results

Blend ID	UNS Blend Formulation					Test Results				
	UNS Sol (mL)	sWheat (mL)	Waste Lock® 770 (mL)	Water:Waste (Volume Ratio)	Zeolite:Waste (Volume Ratio)	SW-846 Test Method 1030	SW-846 Test Method 1050	UN O.1 Testing	UN O.2 Testing	Paint Filter Test Method 9095B
UNS Blend 1	50	0	0	0	0	NA: Solution	NA:Solution	NA: Solution	Not Div 5.1	NA: Solution
UNS Blend 2	50	50	0	0	0	Nonflammable	DOT Packing	Not Div 5.1	NA	No free liquids
UNS Blend 3	50	150	0	0	0	Nonflammable	Not self-	Not Div 5.1	NA	No free liquids
UNS Blend 4	50*	50	0	0	0	Nonflammable	DOT Packing	Not Div 5.1	NA	No free liquids
UNS Blend 5	50*	150	0	0	0	Nonflammable	DOT Packing	Not Div 5.1	NA	No free liquids
UNS Blend 6	50	50	0	0.5:1	3:1	Nonflammable	Not self-	Not Div 5.1	NA	No free liquids
UNS Blend 7	50	150	0	0.5:1	3:1	Nonflammable	Not self-	Not Div 5.1	NA	No free liquids
UNS Blend 8	50*	50	0	0.5:1	3:1	Nonflammable	Not self-	Not Div 5.1	NA	No free liquids
UNS Blend 9	50*	150	0	0.5:1	3:1	Nonflammable	Not self-	Not Div 5.1	NA	No free liquids
UNS Blend 10	50	50	0	0.5:1	2:1	Nonflammable	Not self-	Not Div 5.1	NA	No free liquids
UNS Blend 11	50	150	0	0.5:1	2:1	Nonflammable	Not self-	Not Div 5.1	NA	No free liquids
UNS Blend 12	50*	50	0	0.5:1	2:1	Nonflammable	Not self-	Not Div 5.1	NA	No free liquids
UNS Blend 13	50*	150	0	0.5:1	2:1	Nonflammable	Not self-	Not Div 5.1	NA	No free liquids
UNS Blend 14	50	0	3.12	0	0	NA: Solution	NA: Solution	NA: Solution	Not Div 5.1	NA: Solution
UNS Blend 16	50	0	3.12	0	3:1	Nonflammable	Not self-	Not Div 5.1	NA	No free liquids
UNS Blend 18	50	0	3.12	0	2:1	Nonflammable	Not self-	Not Div 5.1	NA	No free liquids

Notes: DOT = U.S. Department of Transportation. NA = Not applicable.

* pH-adjusted solution (Spilfyter® Kolorsafe®).

5.3.5 Debris Testing

The RNS waste drums contain debris typically composed of plastic, cardboard, rubber gloves, rags, and lead. It is unclear if the debris that has comingled with RNS waste should carry the D001 code for an oxidizer. To examine this aspect of the waste stream, various tests were performed. Samples of the debris types commonly found in RNS waste drums were subjected to environments that simulate the conditions in the RNS drums and tested to see how they respond to SW-846 Test Methods 1030 and 1050. The debris waste evaluated included cardboard liner, plastic bags, rubber gloves, and Wypall® rags.

5.3.5.1 Effect of UNS Liquid on Organic Debris

UNS Surrogate Solution was prepared and used to soak test samples of the different types of debris waste. Cardboard, plastic, rubber glove, and rag samples were submerged for 2 h in the UNS Surrogate Solution and then submitted for SW-846 Test Methods 1030 and 1050. Samples of the cardboard liner, plastic, and rubber glove were soaked and then allowed to drain for 1 h, after which they were submitted for testing. The Wypall® rags were soaked, squeezed to remove excess moisture, and then submitted for testing.

Test results for the debris soaked in UNS Surrogate Solution are presented in Table 9.

5.3.5.2 Effect of RNS Waste on Organic Debris

RNS waste surrogate was prepared using WB8 salt surrogate and sWheat to coat the debris samples. A 1:1 by volume blend of WB8 salt-to-sWheat surrogate was prepared and comingled with the debris to simulate conditions found in the RNS drums.

The WB8 salt-to-sWheat surrogate was impregnated onto the debris samples using a rolling pin. The surrogate RNS material was rolled onto the organic debris in an attempt to impregnate the debris with the RNS surrogate. After the material was rolled, the excess surrogate was shaken off. The debris samples were then submitted for SW-846 Test Methods 1030 and 1050 along with samples of untreated materials.

Test results for the debris impregnated with surrogate RNS material are presented in Table 9.

5.3.5.3 Discussion of Debris Test Results

Debris samples provided by LANL from actual materials used during the preparation of the RNS waste drums were treated with UNS solution and RNS surrogate waste to determine if the materials might be considered ignitable (D001). The conditions the test materials were subjected to were far harsher than what actual materials will endure in the RNS waste drums before they are remediated. The debris was submerged for 2 h during the UNS solution testing and physically impregnated with RNS-blended salt/sWheat material to simulate contamination with RNS waste material. The tested samples were evaluated in duplicate to ensure results could be replicated, unless a positive result was achieved. It is clear from available RTR information that the debris will not encounter free liquids nor will it be forcefully impregnated with RNS waste material before remediation.

All the tested debris material passed the SW-846 Test Methods 1030 and 1050 testing, except the Wypall® rags. This is an expected result because the rags are cellulose-based and are absorbent. Additional testing was conducted that evaluated maceration of Wypall® rags followed by addition of zeolite, demonstrating its effectiveness and these test are discussed in Section 5.3.6.

Table 9
Debris Reactivity Test Results

Debris Type	Debris Treatment	SW-846 Test Method 1030	SW-846 Test Method 1050
Cardboard	None	Nonflammable	Not self-heating
Cardboard	Soak in UNS Sol.	Nonflammable	Not self-heating
Cardboard	Soak in UNS Sol.	Nonflammable	Not self-heating
Cardboard	Comingle with RNS	Nonflammable	Not self-heating
Cardboard	Comingle with RNS	Nonflammable	Not self-heating
Plastic	None	Nonflammable	Not self-heating
Plastic	Soak in UNS Sol.	Nonflammable	Not self-heating
Plastic	Soak in UNS Sol.	Nonflammable	Not self-heating
Plastic	Comingle with RNS	Nonflammable	Not self-heating
Plastic	Comingle with RNS	Nonflammable	Not self-heating
Rubber glove	None	Nonflammable	Not self-heating
Rubber glove	Soak in UNS Sol.	Nonflammable	Not self-heating
Rubber glove	Soak in UNS Sol.	Nonflammable	Not self-heating
Rubber glove	Comingle with RNS	Nonflammable	Not self-heating
Rubber glove	Comingle with RNS	Nonflammable	Not self-heating
Wypall® rag	None	Flammable with rate of 3.52 mm/s	Not self-heating
Wypall® rag	Soak in UNS Sol.	Nonflammable	DOT Packing Group II
Wypall® rag	Soak in UNS Sol.	Nonflammable	No duplicate test
Wypall® rag	Comingle with RNS	Nonflammable	Not self-heating
Wypall® rag	Comingle with RNS	Nonflammable	Not self-heating

5.3.6 Additional Testing Conducted to Ensure the Efficacy of the Proposed Remedy

As noted in sections 5.3.4 and 5.3.5, we identified additional testing needed to ensure the effectiveness of our remedy. These tests include:

- Creation of an oxidizing liquid using sodium nitrate that is both acidic and basic, using addition of nitric acid and sodium hydroxide respectively, and pH adjusting the acidic solution using Kolorsafe Spilfyter®. Results in Table 10.
- Addition of tests that assume the addition of acid neutralizer overshot, requiring addition of base neutralizer to bring down the pH. Results in Table 11.
- Maceration of Wypalls® using a blender, followed by addition of zeolite to demonstrate the effectiveness of the remedy. Results in Table 12.

In all cases, the remedy was demonstrated as being effective in removing the hazardous characteristic.

Table 10. Summary of Additional Testing (Oxidizing Liquids)

Blend ID	Blend Formulation						Test Results				
	$NaNO_3$ Acidic (ml)	$NaNO_3$ Basic (ml)	$NaNO_3$ pH Adj. (ml)	Swheat (ml)	Water Water: Waste Vol Ratio	Zeolite Zeolite:Waste Vol Ratio	SW-846 Test Method 1030	SW-846 Test Method 1050	DOT O.1 Test	DOT O.2 Test	Test Method 9095B (Paint Filter)
Sod Nit A– Zeo 1	50	0	0	0	0	4:1	NA:No Fuel	NA:Solution	Not 5.1	NA	No free liquids
Sod Nit A – Zeo 2	50	0	0	0	0	3:1	NA:No Fuel	NA:Solution	Not 5.1	NA	No free liquids
Sod Nit B – Zeo 1	0	50	0	0	0	4:1	NA:No Fuel	NA:No Fuel	Not 5.1	NA	No free liquids
Sod Nit B – Zeo 2	0	50	0	0	0	3:1	NA:No Fuel	NA:No Fuel	Not 5.1	NA	No free liquids
Sod Nit A pH – Zeo	0	0	50	0	0	4:1	NA:No Fuel	NA:No Fuel	Not 5.1	NA	No free liquids
Sod Nit A pH – Zeo	0	0	50	0	0	3:1	NA:No Fuel	NA:No Fuel	Not 5.1	NA	No free liquids
Sod Nit A Blend 1	50	0	0	50	0.5:1	4:1	Nonflammable	Not self-heating	Not 5.1	NA	No free liquids
Sod Nit A Blend 2	50	0	0	150	0.5:1	4:1	Nonflammable	Not self-heating	Not 5.1	NA	No free liquids
Sod Nit A Blend 3	50	0	0	50	0.5:1	3:1	Nonflammable	Not self-heating	Not 5.1	NA	No free liquids
Sod Nit A Blend 4	50	0	0	150	0.5:1	3:1	Nonflammable	Not self-heating	Not 5.1	NA	No free liquids
Sod Nit B Blend 1	0	50	0	50	0.5:1	4:1	Nonflammable	Not self-heating	Not 5.1	NA	No free liquids
Sod Nit B Blend 2	0	50	0	150	0.5:1	4:1	Nonflammable	Not self-heating	Not 5.1	NA	No free liquids
Sod Nit B Blend 3	0	50	0	50	0.5:1	3:1	Nonflammable	Not self-heating	Not 5.1	NA	No free liquids
Sod Nit B Blend 4	0	50	0	150	0.5:1	3:1	Nonflammable	Not self-heating	Not 5.1	NA	No free liquids
Sod Nit A pH Blend	0	0	50	50	0.5:1	4:1	Nonflammable	Not self-heating	Not 5.1	NA	No free liquids
Sod Nit A pH Blend	0	0	50	150	0.5:1	4:1	Nonflammable	Not self-heating	Not 5.1	NA	No free liquids
Sod Nit A pH Blend	0	0	50	50	0.5:1	3:1	Nonflammable	Not self-heating	Not 5.1	NA	No free liquids
Sod Nit A pH Blend	0	0	50	150	0.5:1	3:1	Nonflammable	Not self-heating	Not 5.1	NA	No free liquids

Table 11. Citric Acid Blends (Wet and Dry Additions)

Blend ID	Blend Formulation							Test Results			
	UNS Sol (ml)	UNS Sol pH Adj. (ml)	Citric acid (ml)	Pig Base (ml)	Swheat (ml)	Water Water: Waste Vol Ratio	Zeolite Zeolite:Waste Vol Ratio	SW-846 Test Method 1030	SW-846 Test Method 1050	DOT O.1 Test	Test Method 9095B (Paint Filter)
UNS Blend 19	0	50	50	0	50	0.5:1	3:1	Nonflammable	Not self-heating	Not 5.1	No free liquids
UNS Blend 20	0	50	0	50	50	0.5:1	3:1	Nonflammable	Not self-heating	Not 5.1	No free liquids

Table 12 - Wypall Blend Formulations

Wypall Blend ID (Wypall mix: zeolite)	Wypall Mixture (ml)	Zeolite (ml)	SW-846 Test Method 1030	SW-846 Test Method 1050	DOT O.1 Test	Test Method 9095B (Paint Filter)
WB1(1:3)	1233	3700	Nonflammable	Not self-heating	Not 5.1	No Free Liquids
WB2(1:4)	925	3700	Nonflammable	Not self-heating	Not 5.1	No Free Liquids
WB3(1:5)	740	3700	Nonflammable	Not self-heating	Not 5.1	No Free Liquids

6.0 CONCLUSIONS

This report briefly summarizes the surrogate testing that was done in support of our understanding of the unremediated and remediate nitrat salt waste forms and included:

1. Small-scale testing sensitivity results that included Automatic Pressure Tracking Adiabatic Calorimetry (APTAC) to evaluate thermal response; impact sensitivity (drop weight impact); friction sensitivity; and sensitivity to electrostatic discharge (ESD).
2. Small-scale testing using Differential Scanning Calorimetry (DSC) coupled with Mass Spectrometry to examine the effect of actinide addition to the thermal sensitivity of the surrogates.
3. Testing demonstrating the effectiveness of two treatment methods proposed to stabilize both the unremediated and remediated nitrate salt waste streams (UNS and RNS, respectively). The two technologies include the addition of zeolite (with and without the addition of water as a processing aid) and cementation.

The testing demonstrates that complex salt mixtures exhibit significant thermal sensitivity, with onset temperatures of as little as 42 °C as measured by APTAC. The surrogates also demonstrate some sensitivity to ESD but are not sensitive to initiation by impact and friction.

Spiking the materials with actinides leads to modest increases in thermal sensitivity and is attributable to reaction chemistry as opposed to radiochemical processes.

Finally, both zeolite addition (with and without water as a processing aid) and cementation were demonstrated as effective remedies for removing the hazardous waste characteristics of ignitability (D001) and corrosivity (D002) for all expected forms of the waste.

Full reports of the testing of each of theses areas are available and referenced within this summary.

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[8] 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.
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[11] G. Brown, "Remediated Nitrate Salt (RNS) Surrogate Formulation and Testing Standard Procedure," PLAN-TA-9-2443 (U), Rev. B
[12] **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.
[13] **Drop Weight Impact (DWI).** DWI is a statistical test to determine the 50% reaction level of a material to impact stimulus. In this test, a fixed volume of material is placed on a sand paper disk on top of a steel anvil. A steel striker is placed on the sample and impacted by a 2.5 kg mass falling from a predetermined height. Microphones record the sound generated by the impact. Sound above the intensity due to a blank sandpaper disk is attributed to a reaction in the material (a GO event). Sound below that intensity indicates no reaction in the material (a NO GO event). Commercial software evaluates the GO and NO GO events and adjusts the required height of the 2.5 kg mass to map out the reaction probability distribution. The 50% level is assessed assuming that the measured reaction is Gaussian.

[14] **Friction Sensitivity.** Friction sensitivity testing is a statistical test to determine the 50% reaction level of a material to impact stimulus. In this test, a fixed volume of material is placed on a ceramic plate on a movable platform. A ceramic pin on a lever arm is lowered onto the sample and weight is added to the arm to produce a predetermined friction force. The platform is forced to move under the pin by a motor and reaction indications are assessed by the instrument operator. Smoke, sound, or black marks on the ceramic are attributed to a reaction in the material (a GO event). Lack of these features indicates no reaction in the material (a NO GO event). Commercial software evaluates the GO and NO GO events and adjusts the required weight to map out the reaction probability distribution. The 50% level is assessed assuming that the measured reaction is Gaussian.

[15] **Electrostatic Spark Discharge Sensitivity (ESD).** ESD is a threshold level determination test that evaluates sensitivity of a material to spark discharge stimulus. In this test, a fixed volume of material is added to a sample holder that insulates the material from everything except the bottom electrode of the platform. A piece of scotch tape is placed over the sample holder, enclosing the sample area. The sample holder is placed on the platform and a needle is charged to a predetermined energy with a capacitor bank. The needle is then pushed through the tape and the energy is discharged to the bottom electrode through the sample. If the sample reacts, gas is generated and the tape is torn and sometimes obliterated. If there is no reaction, the tape is only punctured by the needle. The operator assesses the result of the test and varies the energy over a number of different replicates to determine the energy at which there are 20 consecutive NO GO events with at least one GO event at the next higher energy level. The level of the 20 consecutive NO GO events is reported as the Threshold Initiation Level.

[16] **Vacuum Thermal Stability (VTS).** VTS determines the gas generation of a material when held at isothermal conditions (above ambient). In this test, 200 mg of material are placed in a stainless steel test tube that is then inserted into a heater block set to the desired temperature. The sample tube is instrumented with a pressure transducer and all transducers are read by a computer-interfaced control box. Knowing the volume of the tube and the mass of the sample, the pressure generation during heating can be integrated to determine the volume of gas generated per gram of material. This value is compared to known stable standards for relative evaluation of thermal stability.

[17] **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.

[18] M7-16-6063, Memorandum, *Summary of Remediated Nitrate Salt Surrogate Formulation and Testing*, TO: David J. Funk, ADEP, FROM: Geoffrey Brown, M-7, dated May 3, 2016.

[19] D.M. Wayne, PLAN: Differential Scanning Calorimetry and Mass Spectrometry (DSC-MS) of Remediated Nitrate Salt (RNS) Surrogates (U) (2015).

[20] D. M. Wayne, “Simultaneous Thermal Analysis of Remediated Nitrate Salt Surrogates,” LA-UR-16-23438 (2016).

[21] B. A. Robinson and P. A. Stevens, “Options Assessment Report: Treatment of Nitrate Salt Waste at Los Alamos National Laboratory,” LA-UR-15-27180, Los Alamos National Laboratory, Los Alamos, NM, 2015.

[22] K. Anast and D. J. Funk, “Summary Report of Laboratory Testing to Establish the Effectiveness of Proposed Treatment Methods for Unremediated and Remediated Nitrate Salt Waste Streams,” LA-UR-16-22658 (2016).

[23] G. Walsh, Research Scientist, Energetic Materials Research and Testing Center, New Mexico Institute of Mining and Technology, Socorro, New Mexico (Certified DOT Testing Laboratory), “Results of Oxidizing Solids Testing, EMRTC Report RF 10-13,” prepared for Washington TRU Solutions, LLC, March 12, 2010.

[24] K. Anast, “Engineered Option Treatment of Remediated Nitrate Salts: Surrogate Batch-Blending Testing,” LA-UR-16-21653, Los Alamos National Laboratory, Los Alamos, NM, 2016.

[25] K. Anast, “Engineering Options Assessment Report: Nitrate Salt Waste Stream Processing,” LA-UR-15-28900 (2015).