

**Scientific Investigations on the Chemical Reactivity of Los Alamos  
Remediated Nitrate Salt Wastes – 16540**

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**ABSTRACT**

The February 14, 2014 release of radioactivity at the Waste Isolation Pilot Plant (WIPP) was the result of runaway thermal reactions that occurred in a TRU waste drum containing nitrate salts remediated using an organic absorbent. Experimental and modeling studies performed at LANL indicate that mixtures of metal nitrate salts (oxidizer) with sWheat Scoop<sup>®1</sup> organic kitty litter (fuel) create the potential for exothermic chemical reactions. The use of sWheat<sup>®</sup> absorbent in the processing of nitrate salt wastes can be pinpointed as the critical processing decision that led to the failure of the breached drum in the WIPP repository. The most plausible scenario is that a production of heat, either from low-level chemical reactions or the growth of natural microbes, in concert with mixed metal nitrate salts, bismuth lined glovebox gloves and/or lead nitrates when combined with the sWheat<sup>®</sup> organic kitty litter, generated a series of exothermic reactions that heated and pressurized the drum resulting in the venting of high-temperature gases and radioactive material into the room. Observations and modeling studies indicate that the probability of thermal runaway in another drum has decreased with time since the WIPP event. However, the complexity of the mixtures, ambiguity in procedures such as those used for neutralization, the heterogeneity of the drum contents, and the difficulty of sampling leads to an irreducible level of uncertainty that mandates the exercise of caution in managing RNS wastes. The situation also requires that this waste stream continue to be stored in a temperature-controlled environment and monitored until the waste can be remediated to remove the hazard permanently. We recommend that proposals to treat nitrate salts with organic absorbents of any kind be accompanied by experimental studies to confirm that similarly sensitive mixtures are not inadvertently created over the range of conditions (mixture quantities, moisture content, etc.) anticipated during processing and storage.

**INTRODUCTION**

On February 14, 2014, a release of radioactivity occurred at the WIPP, resulting in distribution via airborne transport of radioactivity within the repository and to the surrounding environment in the vicinity of the facility. Evidence indicated that the breached drum was a TRU waste drum containing nitrate salts remediated using an organic absorbent; the drum, positively identified as having breached, is Drum 68660. In response, LANL implemented additional precautions and controls, including overpacking of the 55-gallon remediated nitrate salt (RNS) waste drums into Standard Waste Boxes (SWBs). RNS waste drums similar to those at LANL had previously been shipped to WIPP, and to the low level radioactive waste facility in

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<sup>1</sup> sWheat Scoop<sup>®</sup> is a registered trademark of Farmers Union Industries, LLC, Redwood Falls, MN.

Andrews, Texas managed by Waste Control Specialists, LLC (WCS). LANL, WIPP, and WCS have taken precautions to protect workers, the public, and the environment. To evaluate the specific cause of the breached drum, LANL embarked on a series of scientific investigations discussed in this paper. Additional technical details are available elsewhere [1].

## **BACKGROUND**

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

Nitrate salt wastes result from aqueous nitric acid processing to recover and purify plutonium [2, 3]. After plutonium recovery, the resulting nitric acid solution contains a number of metal ions that result from the processing operations. These nitric acid solutions were concentrated through distillation until the nonvolatile salts in the evaporator were close to saturation. The hot evaporator *bottoms* were poured into a water-cooled tray, which precipitates nitrate salts and leaves a liquid supernatant. After filtration, the salts were dried by pulling air through the salts using house vacuum for approximately 15 minutes. Salts from the ion exchange processes that retained a green coloration were washed with 3.3 M nitric acid to remove residual plutonium to ensure they met the Economic Discard Limit (EDL) for plutonium. However, nitrate salts derived from oxalate filtrates were not washed with high molarity acid ( $> 2M$ ) because it would accelerate decomposition of any oxalic acid present in the salts and could result in pressurization of the sealed 55-gallon drums containing the salts with oxalate. Because of the entrained and interstitial liquids in the nitrate salts wastes, salts produced through either process have the potential to release free liquids over time.

The final composition of nitrate salts depends on the original process feed that was sent to the evaporator. The evaporator feed included ion-exchange effluent and the filtrate from oxalate precipitation. The majority of these nitrate salt wastes were derived from the ion exchange feed. Veazey and others [4, 5] documented the composition of the evaporator bottoms from each of these processes for waste batches produced between April 1992 and February 1994. Contaminated most often with plutonium and americium, these granular, off-white salts were packaged into plastic bags and placed in containers for temporary, retrievable, onsite storage until a permanent waste facility became available—the WIPP. LANL has used evaporators to concentrate liquids that contain nitrate salts since operations began at the TA-55 Plutonium Processing Facility in 1979. This specific type of TRU waste was generated until 1991, when LANL developed a process to solidify the evaporator bottoms in grout rather than dispose of the nitrate salt waste as granular salts.

A review of the historical feed materials used during the ion-exchange process coupled with a Stream Analyzer (OLI Software) theoretical analysis of solids in the parent drum that produced Drum 68660 revealed a composition of predominantly sodium and/or magnesium nitrate with small quantities of other metal cations

(potassium, iron, chromium or aluminum) in the resulting solids. While these modeling efforts do a reasonable job of producing salt compositions from an historical input stream, how close these models are to the actual composition of Drum 68660 is still unclear.

The majority of LANL's TRU waste is *legacy* waste created before 1999 requiring subsequent remediation to meet current WIPP Waste Acceptance Criteria (WIPP-WAC). One concern for disposal of nitrate salt waste lies in its potential to behave as an oxidizer, defined by the National Fire Protection Association (NFPA) as a material that readily yields oxygen to stimulate the combustion of organic matter. Both  $\text{NaNO}_3$  and  $\text{Mg}(\text{NO}_3)_2$ , the primary constituents of the legacy waste, are defined as oxidizers by the NFPA.<sup>2</sup> TRU oxidizers are prohibited from WIPP (exhibit RCRA Characteristic D001 for *ignitability*). In many parent waste containers with nitrate salt-bearing waste, the salts are saturated, and either originally contained or released free liquids with time. Free liquids are also prohibited at WIPP. Remediation of the 30-year-old waste has therefore focused on reducing the oxidizing potential and absorption of free liquids. The liquids were collected, neutralized as necessary, and mixed with an absorbent (or adsorbent) material. The salts were also mixed with absorbent material to reduce their oxidizing potential.

The Energetic Materials Research and Testing Center (EMRTC) previously tested the most oxidizing mixture of sodium and potassium nitrate salts mixed with zeolite or grout as absorbing materials to establish the concentration at which the most reactive mixture of nitrate salt becomes a non-oxidizer when mixed with either zeolite or grout [6]. The EMRTC study examined both the direct mixing of solid nitrate salts with inert material, and the mixing of liquid material, containing dissolved nitrate salts with inert material. The study determined the percentages at which each mixture was considered a non-oxidizing solid, and led to the recommendation that two (2) gallons of zeolite/kitty litter (subsequently 3) be mixed with every gallon of solid or liquid nitrate salt to help ensure the final mixture met or exceeded EMRTC testing constraints [7]. A common application of zeolite is as an absorbent material for pet litter, hence the recommendation to use zeolite/kitty litter.

The absorbents and neutralizers used in remediation have changed over time, and these changes became the focus for the LANL technical investigation into the radiological release from Drum 68660. Unfortunately, the use of a *zeolite based kitty litter* was not appreciated, that is to say, the inorganic nature of zeolites is what leads to the reduction in oxidizing ability, and such zeolites were never used during the process. Instead, all of the nitrate salt waste was processed with an *organic kitty litter*. A recent evaluation of such salt/kitty litter mixtures indicates that the *organic kitty litter* does not reduce the oxidizing ability of the waste, and in fact, increases the hazards associated with the waste (see below). In addition, a number of different dry and liquid neutralizers were used, a fact that must be considered when investigating the potential for chemical reactions in the drums.

The remediation process called for free liquids to be neutralized and mixed with

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<sup>2</sup> NFPA 430: Code for the Storage of Liquid and Solid Oxidizers, Edition: 2004.

absorbent; consequently, after addition of the base (or acid) to neutralize free liquids, the resulting material was mixed with sufficient kitty litter to absorb the free liquids and the mixture placed into new drums. The solid nitrate salts were then mixed with kitty litter and also added to the new drum. Significant uncertainty exists regarding the actual quantities of sWheat<sup>®</sup> added, since they were not documented). After processing the salt, additional TRU wastes were often added to the drums before they were closed, including lead drum liners, contaminated wiping rags, protective clothing, glovebox gloves, or equipment. After packaging, the daughter drums are radiographed, assayed, tested for flammable gases, data-validated, and certified for shipment to WIPP.<sup>3</sup>

### **TECHNICAL ANALYSIS OF REACTIVITY OF THE RNS WASTE STREAM**

This section summarizes the body of experimental and theoretical/modeling work performed at LANL to understand the reactivity of the LANL RNS wastes.

#### **Headspace gases**

Due to concerns raised about adverse chemical reactions in LANL drums in WIPP Panel 7, LANL initiated a program to measure possible reaction byproducts in headspace gases from nitrate salt wastes and remediated nitrate salt wastes stored in drums at LANL Area G. Changes in gas composition over the nitrate waste and the remediated nitrate wastes could be early indicators of possible chemical reactivity within the drums. As such, chemists began characterizing headspace gases in 55 SWBs containing RNS waste for Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC-MS) and for permanent gases<sup>4</sup> using Gas Chromatography with a Thermal Conductivity Detector (GC-TCD). Hydrogen, methane, carbon monoxide, carbon dioxide, and nitrous oxide were observed.

Elevated concentrations of CO<sub>2</sub> and N<sub>2</sub>O have been observed at concentrations well above normal atmospheric concentrations in some of the 55 SWBs containing RNS-bearing waste drums [8]. These concentrations cannot be explained based on radiolysis of waste drum content (see [1] for an analysis) and suggest that the gases are being produced from chemical reactions and/or biological activity of the organic matter/salt mixtures that make up the waste drum contents. Examples of these reactions include chemical oxidation (corrosion and combustion), oxalate decomposition, and sWheat<sup>®</sup> degradation by chemical or biological processes. N<sub>2</sub>O is believed to result from the oxidation of material contained within the nitrate salt containing waste.

A simple mathematical and numerical model of the headspace gas behavior developed in [8] provides a plausible description of the long-term variations of concentrations of gases such as carbon dioxide and nitrous oxide in the SWB headspace. The model balances a gas generation source term from reactions in the RNS drum with mixing from the outside atmospheric air due to ventilation of the SWB. Good fits to the concentration data for Drum 68685 (a sibling to the drum that breached in WIPP) were

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<sup>3</sup> TRU waste characterization conducted for WIPP certification at LANL is under the auspices of WIPP's Central Characterization Project (CCP).

<sup>4</sup> Permanent gases remain gaseous at standard temperature and pressure.

obtained from the time period in which the RNS drum was placed within the SWB in May of 2014 to February 2015. Figure 1 shows a typical result.

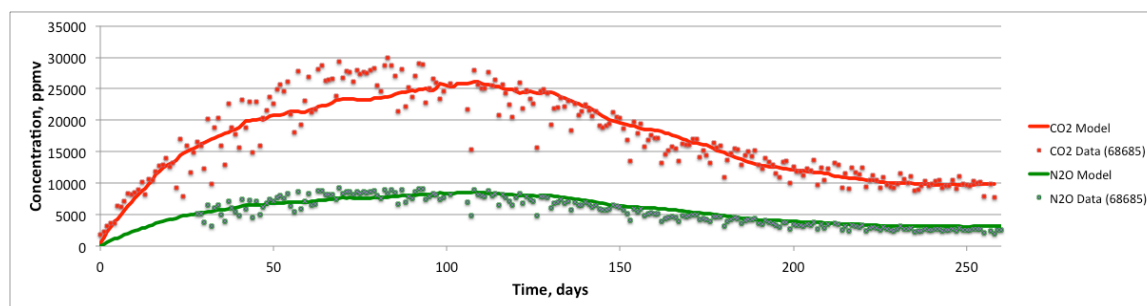


Figure 1 Simulation results compared to data for carbon dioxide and nitrous oxide concentrations for Drum 68685 (from Robinson and Leibman, 2015).

The model results for Drum 68685 suggest a low but persistent level of chemical reaction within the RNS waste drum. Gas generation rates due to reaction are predicted to be a small fraction of the ventilation rates into and out of the SWB, and calculated heat generation rates for a reasonable postulated reaction for the drum (oxidation of sWheat®) are also very low, nominally 1 W or less for the drum. If other reactions are occurring, these could also generate heat, but if they also generate carbon dioxide, this should have been reflected in the form of higher concentrations. Therefore, the level of carbon dioxide in the drums appears to provide a bound on the level of reactivity and heat generation; this bound is very low from a thermal perspective.

The reaction rates exhibit a significant temperature dependence, which explains the higher concentrations of carbon dioxide and other gases in the SWB headspace in the summertime compared to the winter. A model reaction exhibiting an Arrhenius temperature dependence was employed in the model. Calibrations to the data led to values of 15-20 kcal/mol for the activation energy.

Uncertainties in the model have been evaluated to estimate how tightly the model bounds parameters like heat generation rates, given the lack of perfect information on temperatures, available gas volumes inside the SWB and internal drums, and ventilation rates. Reaction and heat generation rates are unlikely to be more than about a factor of two higher than the rates cited above that were derived from the data fit. Other parameter combinations that would lead to higher rates produce simulations that begin to deviate significantly from the observed data.

The drums are currently under temperature control within the Permacon™, and to provide additional margin, supplemental cooling of the facility was implemented. The resulting cooler storage temperatures correlate to even lower concentrations of gases, implying lower reaction rates, as expected due to temperature-dependent reaction kinetics.

### Process changes and chemical reactivity

We found evidence of multiple process changes in the remediation of nitrate salts over

several years. A large number of experiments (described in Appendix 2 of [1]) were devoted to investigating the various chemicals introduced by process changes related to the remediation of nitrate salt wastes, and the possibility that these chemicals can be involved in exothermic chemical reactions. Process chemistry changes involved the use of a wheat-based kitty litter, citric acid and triethanolamine (neutralizers), and Waste Lock<sup>®</sup>.<sup>5</sup> From these process changes, the daughter drums in the nitrate salt waste stream are now known to contain a mixture of oxidizer (nitrate salt) and fuel (organic). However, literature reports indicate that both the amount of oxidizer (c.a. 30 wt%) and the storage temperature is too low to create an exothermic reaction if no other chemicals and processes are present [9].

*sWheat<sup>®</sup>/nitrate salts.* The use of sWheat<sup>®</sup> kitty litter to absorb free liquids and mitigate the oxidizing potential of nitrate salts instead introduced an organic fuel into intimate contact with the nitrate salts and liquids. It is possible that these conditions could lead to hydrolysis reactions that produce secondary materials more flammable than the starting materials, e.g., generation of furfurals. As a result, the addition of sWheat<sup>®</sup> kitty litter with nitrate salts was considered a possible candidate for generating an exothermic reaction in the drum.

A detailed experimental test matrix was developed to evaluate the chemical reactivity of sWheat<sup>®</sup> kitty litter with nitrate salts and nitric acid and to evaluate sensitivity and thermal stability of such mixtures. Standard experimental approaches were used to measure thermal sensitivities and energetics including differential scanning calorimetry (DSC), thermal activity monitor (TAM), and automatic pressure tracking adiabatic calorimetry (APTAC). Typically a DSC was used for screening small samples, and the APTAC was employed for more detailed energetic analysis. These experiments demonstrated that simple mixtures of NaNO<sub>3</sub> and sWheat<sup>®</sup> kitty litter exhibit good thermal stability with an exotherm of c.a. 330 °C (DSC). This behavior is similar to thermal behavior observed for mixtures of NaNO<sub>3</sub> with organic materials studied at PNNL as part of their organic tank waste safety program [10]. As a result of this high temperature, the sWheat<sup>®</sup>/NaNO<sub>3</sub> mixture, by itself, is unlikely to be the material that initiated the exothermic reaction in Drum 68660.

*sWheat<sup>®</sup>/HNO<sub>3</sub> and other metal salts.* The presence of acidic liquids in a number of parent drums raised questions about a potential interaction of sWheat<sup>®</sup> kitty litter with nitric acid or other trace metal nitrate salts. While there are many potential metal salts that could be evaluated, most impurity metal ions are at the ppm level. Other metals (lead, bismuth, tungsten, and lanthanum) may have been introduced at higher levels and all of these metal ions are discussed with possible lower temperature reaction mechanisms below. Eutectics of sodium/magnesium nitrate salt mixtures with sWheat<sup>®</sup> kitty litter show decreased thermal stability, with an onset of thermal activity occurring near 165 °C by DSC. Similarly, mixtures of iron(III) nitrate with sWheat<sup>®</sup> kitty litter show an onset of thermal activity occurring near 154 °C by DSC.

While these temperatures are considerably lower than the ~330 °C observed for exothermic behavior of sodium nitrate/ sWheat<sup>®</sup> mixtures, they are still higher than

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<sup>5</sup> Waste Lock<sup>®</sup> is a registered trademark of M2 Polymer Technologies Inc. West Dundee, IL.

the endogenous temperature of the drum without some mechanism for heating to that temperature. In general, these measurements indicate relatively high barriers to initiation of energetic reactions, and that temperatures in excess of 100 °C above ambient conditions would be required to initiate the reaction. We note that these tests involved the study of enhanced chemical reactivity and thermal instability of the sWheat® kitty litter immediately after mixing. Self-heating and low level chemical reactions may take time to produce more reactive mixtures.

*Triethanolamine (TEA).* Prior to September 2013, a dry-formula acid neutralizer containing sodium carbonate and an organic polymer was employed to neutralize acidic liquids before addition of the organic absorbent. After September 2013, acidic liquids found in parent drums were neutralized with an aqueous formulation of triethanolamine (TEA), absorbed with sWheat® and packaged in daughter drums. TEA reacts with nitric acid to produce triethanolammonium nitrate, (HTEA)NO<sub>3</sub>, a material that has been used in liquid propellant and energetic material formulations (e.g. [11]). TEA is also a reducing agent and incompatible with oxidizers. As a result, the addition of TEA was considered a possible candidate for generating an exothermic reaction in the drum.

The chemical reactivity of TEA and sWheat® with nitrate salts and nitric acid was studied to evaluate their sensitivity and thermal stability. From the experiments conducted, neither the TEA itself, HTEA(NO<sub>3</sub>), nor mixtures with NaNO<sub>3</sub> and sWheat® were found to be thermally sensitive, or show evidence of an exotherm below temperatures of ~225 °C (DSC data), still higher than the endogenous temperature of the drum without some mechanism for heating to that temperature. We do note that waste processing operators (and as expected when neutralizing an acid with base) indicated that heat was generated and gas evolved when mixing the liquid with neutralizers, which may have contributed to other chemical reactions within the drum, potentially generating thermally sensitive materials (described in more detail below).

*Other potential reactive chemicals, including oxalate salts.* Our review of historical data for the drums indicated the potential for the presence of other reactive chemicals that could potentially lower the exothermic threshold for reactivity. This includes the presence of oxalate salts or ammonia (NH<sub>3</sub>) in nitrate salts from evaporator bottoms, the presence of furfurals, carbohydrates, or other small organic molecules from the hydrolysis of the sWheat® cellulosic materials, or the presence of ketones and aldehydes produced in reactions catalyzed by trace quantities of transition metals (e.g., Fe, Ni, Cr). Thermal analyses of a variety of organic wastes (oxalate, citrate, EDTA, etc.), with nitrates and nitrites, have been reported previously [10]: relatively high temperatures (150 - 350 °C) are required to initiate reactions in the nitrate salt/organic mixtures employed.

Oxalate salts decompose in the presence of heat or HNO<sub>3</sub> to generate CO<sub>2</sub> and H<sub>2</sub>O [12, 13]. From the historical evaluation of the known chemical processes, some parent drums contained as much as 50% nitrate salts derived from an oxalate process stream. Consequently, these nitrate salts may contain small amounts of oxalate (3-10%). It is possible that the decomposition and/or oxidation of this minor component of oxalate salts is responsible for the high concentrations of CO<sub>2</sub> in

headspace gases that have been observed in certain drums currently being monitored. Furthermore, the act of reprocessing may have enabled contact of the oxalates with acidic components of the waste stream; thus, accelerating oxalate decomposition.<sup>6</sup> Emptied parent waste drums and headspace gases were analyzed for the presence of these and other chemicals as a potential source for reactive species (Appendix 3 of [1]). Low concentrations of the oxalate anion were observed and recent analysis of the parent of 68660 indicates similar results. We note that the residue in the parent drum is not necessarily representative of the majority of the contents, due to the inhomogeneity of the original waste.

*Citric acid.* Although citric acid could have been employed prior to mixing with sWheat<sup>®</sup> to neutralize alkaline liquids that may have been generated during the neutralization process, it was not documented as having been used in the neutralization of Drum 68660. Given this fact, the potential role of citric acid was not studied experimentally. The behavior of mixtures of sodium nitrate and sodium citrate has been described by others [10].

### Spontaneous self-heating mechanisms

We have established that sWheat<sup>®</sup> kitty litter/ $\text{NaNO}_3/\text{HNO}_3$  combinations can lead to exothermic reactions when heated to temperatures over 300 °C, sWheat<sup>®</sup> kitty litter/ $\text{TEA}(\text{NO}_3)/\text{HNO}_3$  combinations when heated to over 220 °C, and eutectics and other metal nitrate salts show exothermic onsets near 155 °C. However, to explain the breach of Drum 68660 there still must be other mechanisms available that can initiate an exothermic reaction at even lower, more accessible temperatures.

Spontaneous self-heating is the slow chemical reaction of an element or compound that causes the bulk temperature of the element or compound to rise without the addition of an external heat source. For spontaneous ignition to occur, the rate of heat being generated must exceed the rate of heat removal by conduction, convection, and thermal radiation. As the temperature of the material begins to rise, the rate of heat generation will often increase exponentially with temperature, whereas the rate of heat transfer from the material is only linearly dependent on temperature (e.g. [14]). If reaction rates exceed heat transfer rates, the result is a *runaway* reaction that ultimately causes ignition in the presence of oxygen or other oxidizing species. Conversely, if the rate of heat removal exceeds the rate of generation, the material will cool and cannot suffer thermal ignition.

Spontaneous self-heating may be the result of direct oxidation of hydrocarbons (for example, oils, coal, and solvents) or it may be due to action of microorganisms in organic materials. The desire to find a mechanism that would raise the drum contents to temperatures sufficient for thermal runaway led to additional investigations. A number of trace-metal impurities are present in the nitrate salts, and literature studies show that many of them have the potential to lower the barrier to nitration of

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<sup>6</sup> Waste drums contained salts from both the oxalate and lean residue processes, but were stored (initially) in separate bags. Upon processing at WCCRF, the potentially intact bags were broken and the salts mixed, leading to the potential for high molarity acid (from the LR process) to be in contact with the oxalate salt, leading to possible oxalate decomposition.



organics. In addition, recent studies with the expected nitrate salt mixtures have indicated that the salt mixtures themselves are unstable at or near room temperature, leading to vapor generation (nitrogen dioxide, dinitrogen tetroxide) that has been demonstrated to nitrate the sWheat® material, creating a material with greater combustion potential (see discussion on the nitration of organics below).

*Glovebox Glove.* Written records and Real-Time Radiography video indicate that Drum 68660 contained a glovebox glove was added as processing waste from operations at WCRR. Due to the documented history in the DOE Complex of energetic reactions with lead-lined gloves in a nitric acid environment (e.g. [15]), we initiated a detailed set of experiments aimed at assessing the potential for the glove in Drum 68660, which is a newer vintage glove containing Bismuth, Tungsten, and Lanthanum, to exhibit enhanced chemical reactivity. In very high concentrations of nitric acid, the system does exhibit this enhanced reactivity, but as pointed out by the Technical Assessment Team charged with conducting an independent review of the release event [16], the physical separation of the glove from the sWheat®/salt mixture in Drum 68660 makes involvement of the glove in a mechanism for low-temperature reactivity unlikely.

*Lead and bismuth contaminants.* Studies revealed the presence of lead introduced from lead liners in some drums, including Drum 68660. A literature review of the reactivity of lead and bismuth nitrates with organic materials reveals that these nitrate salts have been implemented as sensitizers in dry blasting agent explosive mixtures, as oxidizers for energetic mixtures, and as effective nitrating agents for organic nitration reactions at low temperatures. In particular, several US and international patents or patent applications describe the use of either lead or bismuth nitrates or subnitrates [formed through partial hydrolysis of  $\text{Bi}(\text{NO}_3)_3$ ] as sensitizers and oxidizers in energetic mixtures (e.g. [17, 18]). Also, a US patent was granted [19] for the use of lead nitrate as a sensitizer for dry blasting agents comprised of ammonium nitrate and fuels.

Since a number of nitrate salt waste drums may contain  $\text{HNO}_3$  and lead from drum liners, studies on the formation of explosive mixtures in nitric-acid-contaminated leaded glovebox gloves have relevance even if the glovebox glove itself is unlikely to be involved in the reactions in Drum 68660. Mishra and others [20, 21] reported that treating Neoprene- $\text{Pb}_3\text{O}_4$ -Hypalon layered gloves with 7 M and 12 M nitric acid yielded a residue that exhibited energetic behavior. Motivated by these results, and the historical relationship of lead-lined glovebox gloves to exothermic events in the presence of  $\text{HNO}_3$ , we initiated experiments aimed at assessing the potential for the lead and  $\text{Pb}(\text{NO}_3)_2$  to exhibit exothermic reaction or chemical sensitivity. Studies of solid lead flake and nitric acid with sWheat® kitty litter/ $\text{NaNO}_3$  reported in [1] reveal an exothermic reaction at the lower temperature of 110-120 °C. In summary, studies of the glovebox gloves (Bi, W, La), lead and bismuth nitrates, and nitric acid with sWheat® kitty litter reveal the onset of an exothermic reaction (DSC data) at the temperature of ~100-120 °C.

*Other metal impurities and nitration of organics.* Of significance are the finding of a variety of metal impurities originating from glovebox gloves (containing bismuth, tungsten, and lanthanum), the nitrate salts (principally iron, aluminum, and

magnesium) and lead from lead drum liners used in some drums, including the parent of Drum 68660. Efforts have advanced to the application of process chemistry modeling codes (*Stream Analyzer*) to simulate the original evaporator process, and use thermodynamic properties (solubility products, etc.) to generate an expected composition of nitrate salts. The goal is to have a representative metal nitrate salt – sWheat<sup>®</sup> mixtures run by DSC, and then use the DSC kinetics to improve the fidelity of the model for Drum 68660. Current experimental efforts are focused on the potential for synergistic effects of the combined metal nitrate salts predicted from these models, and to use this composition to guide the development of surrogates in planned full-scale drum tests designed to simulate the conditions expected in 68660. Our studies of nitrate salt mixtures have shown that the mixtures are unstable, decomposing to gaseous products under ambient conditions, generating NO<sub>x</sub> and leading to nitration of the organic sWheat<sup>®</sup> material at a 6 - 7% nitration level – mass % of nitrogen.

The key step in nitration of organics by nitric acid involves the generation of the nitronium ion, [NO<sub>2</sub>]<sup>+</sup>, a potent electrophile, from concentrated nitric acid [22, 23]. Reaction of [NO<sub>2</sub>]<sup>+</sup> with electrons in multiple bonds on the organic substrate leads to product formation (R-NO<sub>2</sub>). Reaction of the nitronium ion with a hydroxyl group will give the nitrate ester (R-ONO<sub>2</sub>). A literature review of metal catalyzed nitration reactions reveals that many metal ions are able to catalyze the nitration of organic materials, especially under conditions where high concentrations of nitric acid are present, with higher nitric acid concentrations favoring the widest variety of metals as catalysts. In the absence of nitric acid, it is even possible for bismuth nitrate to effect the nitration of aromatic compounds. Thus, nitration mechanisms potentially exist as a result of mixing the salts with sWheat<sup>®</sup> and when considering the possible environmental conditions (e.g. low pH, metal ions, etc.), resulting in the possibility of more flammable materials (nitrated sWheat<sup>®</sup>).

*Studies of surrogate salt mixtures.* Kinetic modeling efforts revealed the potential for a runaway reaction with lead and sodium nitrate mixtures, when a simple Arrhenius kinetic relationship is assumed for the chemical reaction processes. In order to simulate the worst-case scenario with no heat exchange with the surroundings, we turned to the use of an APTAC, offering the capability to quantitatively measure changes in temperatures, enthalpy, and pressure. The use of adiabatic systems has the advantage that no heat loss is allowed from the sample, affording the ability to simulate the behavior in a real larger-scale system.

Starting with the *Stream Analyzer* models of the original evaporator process, a general mixed salt composition was generated. A series of surrogate RNS wastes were then created by mixing salts of varying composition with sWheat<sup>®</sup>, HNO<sub>3</sub> and water to simulate the composition of RNS wastes. Samples differed in the amount of iron, magnesium, moisture, etc. and the energetics of reaction was evaluated by APTAC. The series of mixtures studied to date demonstrate that iron is key to producing NO<sub>2</sub> from these surrogates, and that nitration of the sWheat<sup>®</sup> kitty litter with NO<sub>2</sub> leads to the onset of a low temperature exotherm. At this time is unclear whether other metal ions assist in the sWheat<sup>®</sup> nitration reaction. Lower amounts of water (waters of hydration of metal nitrate salts) seem to be associated with ease of nitration.

An example record from an APTAC experiment of a surrogate waste composition that shows evidence for a runaway reaction is shown in Figure 2. This sample shows clear evidence of self-heating as seen in the bottom figure, where an exotherm begins near 60 °C at approximately 360 minutes into the experiment. During this exotherm the pressure increases to near 30 psi (top figure). The internal exotherm results in a temperature increase from 60 – 100 °C over a very short time duration, followed by a runaway reaction that quickly takes the temperature to 250 °C, and the pressure to 127 psi. Removal of iron gives a result with no evidence of self-heating. Studies of this kind have been essential in guiding studies of surrogate compositions for full-scale testing and modeling, as well as development of treatment methods for this waste.

*Other Studies.* Experimental and modeling work is presently underway to evaluate the role that spontaneous self-heating due to biological or chemical processes may have played. Pending completion of ongoing work, it is plausible to consider that some level of chemical and/or biological activity could be taking place inside the kitty litter/ $\text{NaNO}_3$  mixture and this activity could contribute to self-heating of the waste. At temperatures below ambient, any such activity in the waste, whether chemical or biological, would be significantly reduced, preventing self-heating from occurring.

Regardless of whether the self-heating is due to biological or low-level chemical reactions, there is a need to examine the potential thermal behavior of the waste in the configuration of a waste drum. Both numerical modeling and full-scale testing with non-radioactive surrogate material are ongoing to explore the possible conditions that led to the breach of Drum 68660. Findings from these studies will be reported separately. In summary, temperature, pressure, thermal transport conditions, and reaction thermodynamics and kinetics all play important roles in explaining the reasons for the drum breach, as well as the reasons that no other drum has failed.

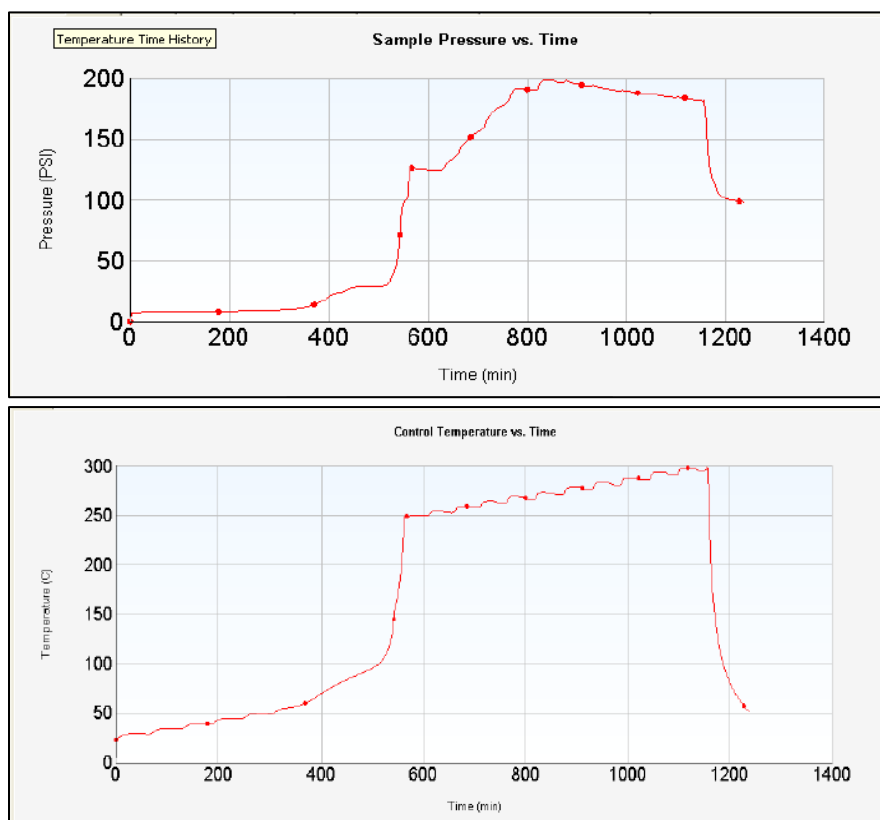
## DISCUSSION AND CONCLUSIONS

Several key findings were identified from the literature review and the extensive set of chemical reactivity studies and modeling efforts. These findings are being used as a basis for decisions regarding the storage and eventual treatment of the RNS wastes both at LANL and WCS.

1. ***The nitrate salt/ sWheat<sup>®</sup> organic kitty litter mixture creates the potential for an exothermic reaction and breach in Drum 68660.***

Experimental and modeling studies indicate that simple mixtures of metal nitrate salts (oxidizer) with sWheat<sup>®</sup> organic kitty litter (fuel) create the potential for exothermic chemical reactions. Our studies indicate that relatively high temperatures are required, even in the presence of triethanol-ammonium nitrate (TEAN), and we find no evidence for runaway exothermic reactions of these simple mixtures below approximately 160 °C. Other studies reported in the literature indicate that similarly high temperatures (150 - 350 °C) were required to initiate reactions in the simple nitrate salt/organic mixtures of that study. However, we have found that complex salt mixtures can generate low temperature (60 °C) thermal onsets similar to that reported in [24]. Evaluation of Drum 68660 characteristics coupled with extensive

chemical testing indicate that, in addition to the nitrate salt/ sWheat<sup>®</sup> mixture, an additional low-temperature chemical reaction mechanism (or mechanisms) is likely required to raise the internal drum temperature high enough to initiate the nitrate salt/ sWheat<sup>®</sup> organic kitty litter mixture.



*Figure 2 APTAC experimental run of an RNS surrogate test sample that provides evidence for thermal runaway reaction. Pressure evolution with time is shown in the top figure, and temperature evolution with time is shown in the bottom.*

**2. An additional chemical reaction mechanism is likely required to provide the self-heating chemical reactions needed to breach a drum.**

We have demonstrated that the temperatures needed to initiate chemical reactivity may be substantially lowered when a combination of conditions exist. We have identified a range of chemical conditions including initial high acid concentration of free liquids, significant quantities (> 1 gal) of neutralized, absorbed free liquids, the presence of reactive or catalytic metals like magnesium, iron, or lead, the presence of bismuth containing glovebox gloves, and lower-temperature chemical or biological reactions that could lead to chemical reactivity at substantially lower temperatures.

In the search for potential low-temperature mechanisms, it was determined that mixtures of metal nitrate salts with HTEA(NO<sub>3</sub>) (TEAN) do not result in exothermic behavior below 220 °C. However, complex mixtures of metal ions, particularly iron and magnesium, can generate NO<sub>2</sub> that facilitates the nitration of sWheat<sup>®</sup>. **These**

***complex salt mixtures produce exothermic behavior as low as 60 °C.*** While encouraging for understanding factors that may lead to the breach of a drum, it is still important to understand how a drum could, through spontaneous self-heating, reach a temperature of 60 °C (140 °F), which is still well above the expected temperature conditions experienced by a drum in the absence of self heating.

***3. Our current working hypothesis and event description is as follows: Spontaneous self-heating, either from low-level chemical reactions or the growth of natural microbes, in concert with mixed metal nitrate salts, bismuth lined glovebox gloves and/or lead nitrates when combined with the sWheat<sup>®</sup> organic kitty litter, generated a stepwise series of exothermic reactions that heated and pressurized the drum resulting in the venting of high-temperature gases and radioactive material into the room.***

A notional ladder of exothermic reactions, leading to the possibility of bulk reaction of nitrate salts with the sWheat<sup>®</sup> absorbent that was added during the remediation process, is shown in Figure 3.

Under this scenario, the contents and reactions inside the drum are sufficient to lead to the increased temperature and pressure that eventually led to failure of the drum: it is not necessary to invoke an external heat source to explain the event. However, sWheat<sup>®</sup> absorbent is the common ingredient in all reactions depicted in Figure 3, so that even if an external heat source was present, the commingling of sWheat<sup>®</sup> (fuel) and nitrate salts (oxidizer) created a temperature-sensitive mixture with the potential for exothermic reaction leading to drum failure. Therefore, the use of sWheat<sup>®</sup> absorbent in the processing of nitrate salt TRU wastes can be pinpointed as the critical processing decision that led to the failure of Drum 68660, regardless of the details of the thermal processes that enabled the drum to achieve temperatures sufficient for thermal runaway.

Obviously, the use of sWheat<sup>®</sup> in this fashion was ill advised. More broadly, we recommend that proposals to treat nitrate salts with organic absorbents of any kind be accompanied by experimental studies to confirm that similarly sensitive mixtures are not inadvertently created. Those studies should be performed over the range of conditions (mixture quantities, moisture content, etc.) anticipated during processing and storage.

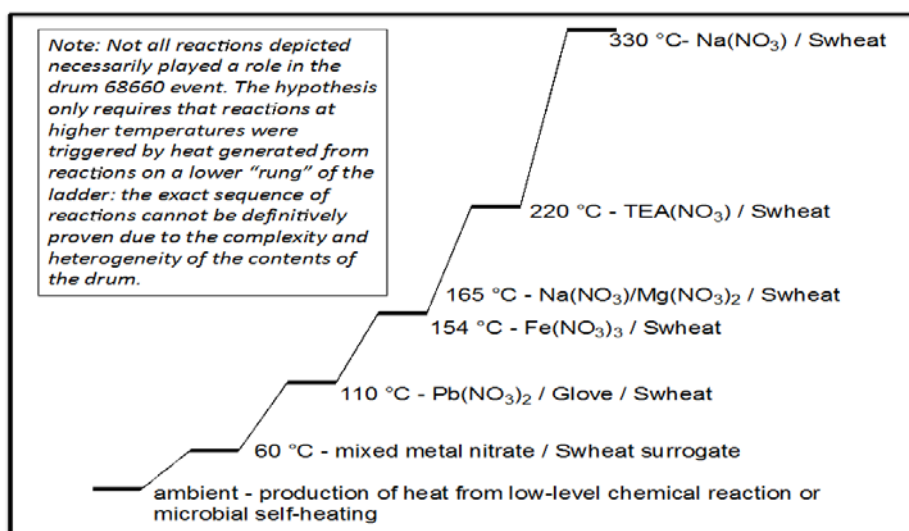


Figure 3 Notional ladder of stepwise chemical or biological reactions that may increase the temperature inside a drum.

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