LA-UR-15-22393

Title: Chemical Reactivity and Recommended Remediation Strategy for Los Alamos Remediated Nitrate Salt (RNS) Wastes

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Intended for: Report

Issued: 2015-04-02

Chemical Reactivity and Recommended Remediation Strategy for Los Alamos Remediated Nitrate Salt (RNS) Wastes

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February 17, 2015

EXECUTIVE SUMMARY

Nitrate salt wastes were generated during historical processing operations to recover and purify plutonium at Los Alamos National Laboratory (LANL). These nitrate salts have the potential to behave as oxidizers, and to contain entrained liquids, both of which are prohibited in the Waste Isolation Pilot Plant (WIPP). A process was developed to remediate nitrate salts by mixing salts with an *inorganic* zeolite pet litter to absorb free liquids, and remove the oxidizing characteristic of the wastes. Process changes introduced instead an *organic* wheat-based pet litter along with *organic* neutralizers, generating a new waste form referred to as Remediated Nitrate Salt (RNS) waste. The February 2014 radiological release at the WIPP site was traced to a LANL RNS waste drum number 68660.

Experimental and modeling studies performed at LANL indicate that mixtures of metal nitrate salts (oxidizer) with Swheat organic kitty litter (fuel) create the potential for exothermic chemical reactions. Even in the presence of triethanol-ammonium nitrate (TEAN) created during neutralization, relatively high temperatures, greater than approximately 160 °C (320 °F), are required for runaway exothermic reactions. Evaluation of Drum 68660 characteristics coupled with extensive chemical testing indicate that, in addition to the nitrate salt/Swheat organic kitty litter mixture, an additional trigger mechanism (or mechanisms) is likely required to raise the internal drum temperature high enough to initiate the nitrate salt/Swheat organic kitty litter reaction.

A combination of chemical conditions were identified that may lower the temperature for reaction, 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 the presence of natural biological activity. Complex surrogate nitrate salt mixtures prepared to simulate wastes, particularly those containing iron and magnesium, can generate NO_x gases that partially nitrate the organic Swheat kitty litter and form a more energetic fuel. These complex surrogate salt mixtures display exothermic behavior at temperatures as low as 60 °C (140 °F) which is still well above the ambient temperature conditions experience by a drum. Neutralization of free liquids, and sorption onto Swheat establishes conditions (moisture with near-neutral pH) that will support natural biological activity. Spontaneous self-heating generated by low-level chemical reactions and/or the respiration of bacteria, molds, and microorganisms is potentially important in the early stages and may be sufficient to raise the temperature as high as 60 °C (140 °F), where the other exothermic chemical reactions can take place. Additional studies are being conducted to evaluate the role biological activity may have played in initiating the event. The use of Swheat absorbent in the processing of nitrate salt 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 to initiate the chemical reactions.

From the combined results of literature studies, modeling, and experiments amassed to date, one can arrive at a plausible scenario in which 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 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.

The combined experimental and modeling efforts point to a strategy for safing and remediating the RNS wastes and the remaining unremediated nitrate salt drums. Temperature is a powerful tool for control of both biological and chemical reactivity, and we recommend a *cold-dry strategy* for disposition of RNS waste drums. Cooling drums to -10 °C or lower will slow down or stop both chemical and biological reactivity. Drums can then be warmed back to +10 °C, a value that is 50 °C below the onset temperature of exothermic reactions, consistent with chemical industry safety guidelines for process operating conditions for exothermic reactions. Drums can be processed by removing debris, and the RNS waste mixed into an inorganic matrix of natural mineral zeolite like clinoptilolite. The quantity of zeolite used will need to be determined through reactivity studies. If for some reason, natural zeolites are found to be undesirable, then grout is an acceptable alternative with the important caveat that following water addition to make grout, the wetted nitrate salt/Swheat organic kitty litter mixture should be processed directly into concrete in a timely manner.

1.0 BACKGROUND

1.1 Historical Generation of TRU Nitrate Salt Waste

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

Nitrate salt wastes result from aqueous nitric acid processing to recover and purify plutonium.[1] After plutonium recovery, the resulting nitric acid solution contains a number of metal ions that result from the processing operations. These nitric acid solutions were concentrated through distillation until the nonvolatile salts in the evaporator were close to saturation. According to procedures, 500 to 600 L of feed was reduced to 10 to 25 L of "bottoms". The hot evaporator "bottoms" were poured into a water-cooled tray, 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. Regardless of whether the salts underwent a final wash, or not, because of the entrained and interstitial liquids in the nitrate salts wastes, they 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 LANL MIN02 wastes were derived from the ion exchange feed. Veazey et al. documented the composition of the evaporator bottoms from each of these processes for waste batches produced between April 1992 and February 1994.[2] The solution concentrations[3] of the major metal ions from the lean residue (e.g., residues low in plutonium concentration such as sand, slag, and crucibles) are shown in Table 1. Contaminated most often with plutonium and americium, these granular, off-white salts were packaged into plastic bags and placed in containers for temporary, retrievable, onsite storage until a permanent waste facility became available—the Waste Isolation Pilot Plant (WIPP). LANL has used evaporators to concentrate liquids that contain nitrate salts since operations began at the TA-55 Plutonium Processing Facility in 1979.[1] This specific type of TRU waste was generated until 1991, when LANL developed a process to solidify the evaporator bottoms in grout rather than dispose of the nitrate salt waste as granular salts.

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

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

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

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. Relative to the solution concentrations in Table 1, only minor amounts of calcium are observed in the solids. This can be traced to the high solubility of calcium nitrate relative to the other metal salts present in the evaporator, such that upon concentration of the evaporator solution, calcium ions remain in solution while other ions precipitated as nitrate salts. We note that 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.

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

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

1.2 Remediation of Nitrate Salt Wastes

The vast majority of LANL's TRU waste is "legacy" waste created before 1999 that required subsequent remediation to meet current WIPP Waste Acceptance Criteria (WIPP-WAC).[4]

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 $NaNO_3$ and $Mg(NO_3)_2$, the primary constituents of the legacy waste, are defined as oxidizers by the NFPA.[5] 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

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[4] WIPP-WAC defines conditions for disposal at WIPP, including container, radiological, physical, and chemical properties. http://www.wipp.energy.gov/library/wac/WAC.pdf

[5] NFPA 430: Code for the Storage of Liquid and Solid Oxidizers, Edition: 2004

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.

Table 2. Changes in the absorbent materials used in remediation of nitrate salt waste.*

Absorbent Name	Dates Used	Quantity Purchased (pounds)	Notes
Waste Lock 770	September 2011 to March 2012	Not Available	Composed of Cross-linked polyacrylate. Used at WCRRF before September 2012 for other types of TRU waste
Swheat Kitty Litter	October 2012 to April 2014	43,981	Composed of ground wheat. On average, ~ 2,500 lb./month purchased (range of ~ 50 to ~ 7,800 pounds/month). Used exclusively after July 2013
Yesterday's News Kitty Litter	October 2012	60	Composed of recycled newspaper. One-time purchase
Blue Buffalo Kitty Litter	October 2012	34	Composed of pelleted compressed pine. One-time purchase
ExquisiCat Pine Litter	October 2012	160	Composed of walnut shell. One-time purchase
Feline Pine Litter	November 2012	200	Composed of walnut shell. One-time purchase
Tidy Cat Kitty Litter	July 2013	28	Composed of clay. One-time purchase; approximately half used for a drum that did not contain nitrate salts

*Reported by Energy Solutions International

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[6] G. Walsh, Research Scientist, Energetic Materials Research and Testing Center, New Mexico Institute for 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.

[7] LANL-Carlsbad Office Difficult Waste Team, "Amount of Zeolite Required to Meet the Constraints Established by the EMRTC Report RF 10-13: Application to LANL Evaporator Nitrate Salts", May 8, 2012.

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 MIN02 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). Table 2 shows the change history of absorbents used in this processing to remediate nitrate salt wastes at Los Alamos; Table 3 shows the change history of dry and liquid neutralizers used.

Table 3. Changes in the neutralizer products used in remediation of nitrate salt waste.*

	Product Name	**Dates Used**
Acid Neutralizer	Chemtex Acid Neutralizer – Dry Formula containing sodium carbonate	Prior to September 2013
	Spilfyter Kolorsafe Acid Neutralizer – Liquid Formula containing triethanolamine (TEA)	Exclusively after September 2013
Base Neutralizer	Spilfyter Kolorsafe Benchtop Kits - Anhydrous Citric Acid	Prior to April 2013
	Pig Base Encapsulating Neutralizer – Dry Formula containing citric acid	Exclusively after April 2013

*Reported by Energy Solutions International.

The remediation process called for free liquids to be neutralized and mixed with 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 (Table 2) and the mixture placed into new drums. The solid nitrate salts were then mixed with kitty litter and also added to the new drum. Analysis indicates that the ratio of the mass of kitty litter to nitrate salt used in 68660 was closer to 1:1, based on mass balance of the contents in the drum.[8] Since significant uncertainty exists regarding the actual quantities of Swheat added (they were not documented), the worst-case mixtures need to be evaluated when considering reprocessing. After processing the salt, additional TRU wastes were often added to

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[8] Obtained from mass balance analysis of the siblings 68660 and 68665.

the drums before they are closed, such as lead drum liners, contaminated wiping rags, protective clothing, glovebox gloves, or equipment.

The daughter drums are radiographed; assayed; tested for flammable gases; data validated; and certified for shipment to WIPP.[9]

2.0 TECHNICAL ANALYSIS OF REACTIVITY OF LANL'S REMEDIATED NITRATE SALT WASTE STREAM

2.1 Analysis of Potential Chemical Reactivity

2.1.1. Headspace Gas

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 25 drums and 55 standard waste boxes (SWBs) containing remediated and un-remediated nitrate salt waste for Volatile Organic Compounds (VOCs) by Gas Chromatography/Mass Spectrometry (GC-MS) and for permanent gases[10] using Gas Chromatography with a Thermal Conductivity Detector (GC-TCD). Hydrogen, methane, carbon monoxide, carbon dioxide, and nitrous oxide were observed.

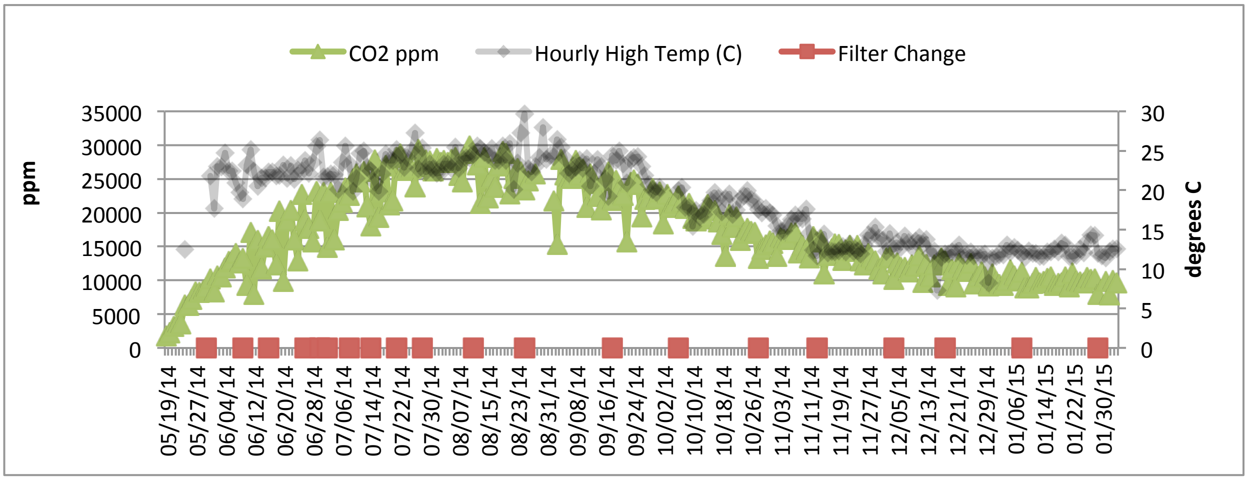

Figure 1. CO_2 Concentration and Maximum Hourly Temperature vs. time for the SWB that contains 68685.

Elevated concentrations of CO_2 and N_2O have been observed at concentrations well above normal atmospheric concentrations in some of the 55 SWBs containing RNS-bearing waste drums (**Appendix 1**, and Figure 1). These concentrations cannot be explained based on radiolysis of waste drum content (section 2.1.2) 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

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[9] TRU waste characterization conducted for WIPP certification at LANL is under the auspices of WIPP's Central Characterization Project (CCP).

[10] Permanent gases remain gaseous at standard temperature and pressure.

reactions include chemical oxidation (corrosion and combustion), oxalate decomposition, and Swheat (organic kitty litter) degradation by chemical or biological processes.[11] N_2O is believed to result from the oxidation of material contained within the nitrate salt containing waste. The N_2O concentrations observed, ranging from (100 – 9000 ppmv), are well above the normal atmospheric concentration of ~ 350 ppbv. The CO_2 concentrations observed (300–45,000 ppmv), are well above the normal atmospheric concentration of ~ 400 ppmv. Gas analysis of the subset of 7 SWBs exhibiting highest concentrations of CO_2 and N_2O are summarized in **Appendix 1**.

2.1.2. Radiation chemistry

Radiolysis of organic materials and water in drums can produce hydrogen, as well as other gases, with the potential to increase pressure, heat, or both inside RNS drums (e.g. 68660). However, extensive experience from LANL and Rocky Flats,[12] including recent radiolysis calculations, suggest that gas generation and heating from radiolysis should be minor based on the radionuclide inventory of Drum 68660, especially over the short, several month time-frame (ca. 75 days) between packaging at LANL and radiological release from Drum 68660 at WIPP.

Typical gas production from radiolysis is dominated by the production of H_2 (though some production of peroxide is expected). This product is the only gas produced in neat water and only small amounts of CH_4 or CO_2 are observed in typical organic radiolysis. Radiochemical modeling suggests that typical drum contents (43 g plutonium and americium ingrowth) will generate *ca*. 0.5 Watts of thermal power,[13] and *ca*. 1 atmosphere of H_2 per 30-day period in head spaces with 4 kg H_2O present in the drum.

Hydrogen is typically the predominant gas produced in the radiolysis of organic materials. Sometimes one will find much smaller yields of CH_4 or other hydrocarbon gases. Ryan found the molar ratio of CO_2 to H_2 to be about 0.7:1.0 in the radiolysis of cellulose.[14] A worst-case analysis, using polyvinyl chloride as the radiolytic source, suggests that the largest molar ratio expected of CO_2 to H_2 could be about 6.5:1. This value for CO_2 production, while larger than expected, is still much lower than that observed by headspace analysis in drums under surveillance, which has been observed to exceed 100:1 for specific drums. The simple conclusion is that the elevated observed concentrations of CO_2 are not due to radiolysis alone.

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[11] Recent measurements of head space gases from surrogates made from Swheat, water, rock salt and debris have exhibited very high concentrations of carbon dioxide without the presence of nitrous oxide consistent with the hypothesis of multiple mechanisms leading to CO_2 generation.

[12] W. V. Conner, "Evaluation of Residue Drum Storage Safety Risks" June 17, 1994, RFP-4826.

[13] LA-UR-14-24117 "Use of analytical chemistry data to estimate the Am/Pu ratio in nitrate salt drums produced by TA-55" D.K. Veirs, Table 6 estimates that there was 38.75 g of Pu and 4.41 g of Am-241 in the parent drum of 68660. The specific wattage for Am-241 is 114.7 W/kg and for Pu-239 is 1.9 W/kg. Normally weapons grade up is 2.1 W/kg due to the presence of the other isotopes. This results in 0.58 W total for the parent drum that is a maximum value for 68660.

[14] J. P. Ryan, "*Radiogenic Gas Accumulation in TRU Waste Storage Drums*," Report DP-1604, Savannah River Laboratory, 1982.

2.1.3. Process changes and chemical reactivity

We found evidence of multiple process changes in the remediation of nitrate salts over several years. The addition of organic materials (potential fuels) with nitrate salts (potential oxidizers) could lead to exothermic chemical reactions. A large number of experiments (**Appendix 2**) were devoted to investigating the various chemicals introduced by process changes related to the remediation of nitrate salt wastes. Process chemistry changes involved the use of a wheat-based kitty litter, citric acid and triethanolamine (neutralizers), and Waste Lock, all of which represent the introduction and mixing of organic material with the nitrate salts. From these process changes, the daughter drums in the MIN02 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 weight %) and the storage temperature is too low to create an exothermic reaction if no other chemicals and processes are present.[15]

- ***Swheat™ organic kitty litter***

Swheat/Nitrate Salts. The use of Swheat 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 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 kitty litter with nitrate salts and nitric acid and to evaluate sensitivity and thermal stability of such mixtures (**Appendix 2**). 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 $NaNO_3$ and Swheat 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 $NaNO_3$ with organic materials studied at PNNL as part of their organic tank waste safety program.[16] As a result of this high temperature, the Swheat/$NaNO_3$ mixture, by itself, is unlikely to be the material that initiated the exothermic reaction in Drum 68660.

Swheat/HNO_3 and other metal salts. The presence of acidic liquids in a number of parent drums raised questions about a potential interaction of Swheat kitty litter with nitric acid or other trace metal nitrate salts. A large number of experiments (vide supra) showed that mixtures of Swheat with HNO_3 and sodium nitrate salts are not chemically sensitive and exhibit an onset of exothermic behavior at

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[15] G. A. Beitel, "*Sodium Nitrate Combustion Limit Tests*," Report ARH-LD-123, April, 1976 Hanford Waste Engineering Plant

[16] R. D. Scheele, R. L. Sell, J. L. Sobolik, L. L. Burger, "Organic Tank Safety Project: Preliminary Results of Energetics and Thermal Behavior Studies of Model Organic Nitrate and/or Nitrate Mixtures and a Simulated Organic Waste", Pacific Northwest National Laboratory, 1995, PNL-10213

temperatures near 330 °C using Differential Scanning Calorimetry (DSC).[17] While there are many potential metal salts that could be evaluated, most impurity metal ions are at the ppm level, with the exception of those listed in Table 1. Other metals (lead, bismuth, tungsten, and lanthanum) may have been introduced at higher levels and all of these metal ions are discussed with possible trigger mechanisms below. Eutectics of sodium/magnesium nitrate salt mixtures with Swheat 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 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 mixtures, they are still higher than 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, and samples prepared to monitor the effect of time on such mixtures are under investigation.

- ***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 absorbent kitty litter. After September 2013, acidic liquids found in parent drums were neutralized with an aqueous formulation of triethanolamine (TEA),[18] absorbed with Swheat kitty litter, and packaged in daughter drums.[19] Triethanolamine reacts with nitric acid to produce triethanolammonium nitrate, (HTEA)NO_3, a material that has been used in liquid propellant and energetic material formulations.[20] 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 kitty litter 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_3), nor mixtures with $NaNO_3$ and Swheat kitty litter were found to be thermally sensitive, or show evidence of an exotherm below temperatures of ~225 °C (DSC data),[21] 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)

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[17] WX-7 Analytical Report #51934 (May, 2014), Los Alamos National Laboratory

[18] May 19, 2014 Energy Solutions memo from Miles Smith to Dan Cox entitled "*Correction to Transmittal of Neutralizers Used in Nitrate Salt Processing*."

[19] WCRRF procedure EP-WCRR-WO-DOP-1198, section 10.3

[20] See for example, U.S. Patent, 3,401,067, Sept. 10, 1968, "Aqueous Slurry Type Explosive Compositions Sensitized with at Least One Alkanolamine Nitrate," and H. Lee and T.A. Litzinger, "Thermal Decomposition Of Han-Based Liquid Propellants," Combustion and Flame, 127:2205–2222 (2001) and references therein.

[21] WX-7 Analytical Report #51933 (May, 2014), Los Alamos National Laboratory, and Bracuti AJ, "The Crystal and Molecular Structure of Triethanol-Ammonium Nitrate'" U.S. Army Research, Development and Engineering Center, Picatinny, NJ. Technical Report ARAED-TR-92026 (1992).

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 (see nitration of organics 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_3) 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). In addition, we cannot rule out the presence of other organics that may have been present in the waste stream from vials, pipettes, etc. (though the likelihood is exceedingly small). These chemicals could react with residual nitric acid in the drums to create reactive species. Thermal analyses of a variety of organic wastes (oxalate, citrate, EDTA, etc.), with nitrates and nitrites, have been reported previously. That study indicated that relatively high temperatures (150 - 350 °C) were required to initiate reactions in the nitrate salt/organic mixtures employed.[16]

Oxalate salts decompose in the presence of heat or HNO_3 to generate CO_2 and H_2O.[22,23] 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_2 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.[24] 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**). Low concentrations of the oxalate anion were observed and recent analysis of the parent of 68660 indicates similar results.[25] 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***

Citric acid could have been employed to neutralize alkaline liquids prior to mixing with kitty litter and it is possible that it was used to acidify the liquid nitrate salts if the operator overshot the target pH of 5-7 using the acid neutralizer (TEA). However, the majority of waste drums were acidic, so citric acid was used infrequently relative to triethanolamine. Citric acid was not documented as having been used in

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[22] M. Kubota, "*Decomposition of Oxalic Acid with Nitric Acid*," *J. Radioanal. Chem. 75*, 1982, pp 39-49.

[23] D. A. Turner, Y. Miron, "Testing of Organic Waste Surrogate Materials in Support of the Hanford Organic Tank Program – Final Report", 1994, Westinghouse Hanford Company, WHC-MR-0445.

[24] 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.

[25] B. Chamberlin and P. Martinez, LANL, see Appendix 3.

the neutralization of Drum 68660, and while the documentation was sparse,[26] 68660 was documented as having a pH of 0, and therefore it is very unlikely that citric acid was used.

There are no current tests being conducted with citric acid. The behavior of mixtures of sodium nitrate and sodium citrate has been described by others.[16]

- ***Waste Lock***

Waste Lock® was initially used to absorb free liquids and introduced a source of organic material (fuel). Subsequently, a new procedure was implemented to absorb liquids by employing Kitty litter (i.e. remediate wastes by adding a different absorbent). Given that Drum 68660 did not contain Waste Lock® and that Waste Lock® was not used after March 2012, we have not focused on this potential at this time, and no experiments are currently planned using Waste Lock®.

2.1.4. Trigger mechanisms

We have established that Swheat kitty litter/$NaNO_3$/HNO_3 combinations can lead to exothermic reactions when heated to temperatures over 300 °C, Swheat kitty litter/TEA(NO_3) /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 trigger mechanisms available that can initiate an exothermic reaction at even lower, more accessible temperatures. We note that previous studies have shown that complex mixtures of wastes can exhibit greater thermal sensitivity than the individual components.[16]

This caused LANL chemists to focus on potential trigger mechanisms in addition to the ongoing length of time studies, which could produce heat, lower the temperature required for an exothermic reaction, or both. 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 organics. In addition, recent studies with the expected nitrate salt mixtures (see "Summary of metal impurities" below) 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 "Nitration of organics" below).[27]

- ***Glovebox glove***

Written records indicate that Drum 68660 contained a glovebox glove added as processing waste from operations at WCRR.[28] Confirmation of the presence of the glovebox glove was obtained from a review of the Real-Time Radiography video created as part of the Waste Certification process. In current practice, these gloves would most likely be bismuth-lined (gloves that contain a mixture of bismuth (Bi), tungsten (W), and lanthanum (La) as opposed to older lead-lined gloves that were historically used

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[26] Documentation was not required or specified for waste nitrate salt processing.

[27] Recent work with salt mixtures (as described later in the text) has demonstrated that the decomposition of the salts to generate NO_2/N_2O_4 will nitrate the Swheat to the 6-7% level, increasing its flammability (LANL, WX-7, unpublished results).

[28] May 20, 2014 Energy Solutions memo from Miles Smith to Dan Cox entitled "Revision 1, Nitrate Salt Waste Containers at WCS, WIPP Panel 7, and LANL Data Summary."

around the DOE Complex. Purchase records confirmed that bismuth-lined gloves were used at WCCRF during remediation of nitrate salt wastes. We note that lead-lined gloves in a nitric acid environment have led to energetic events at Rocky Flats,[29] Mound,[30] and Los Alamos,[31] and therefore, the presence of a glovebox glove required additional evaluation.

As a result of the historical relationship of glovebox gloves to exothermic events in the presence of HNO_3, we initiated a detailed set of experiments aimed at assessing the potential for the current bismuth-lined glovebox gloves, and the elements associated with their interior lining (Bi, W, La), to exhibit an exothermic reaction or show chemical sensitivity.

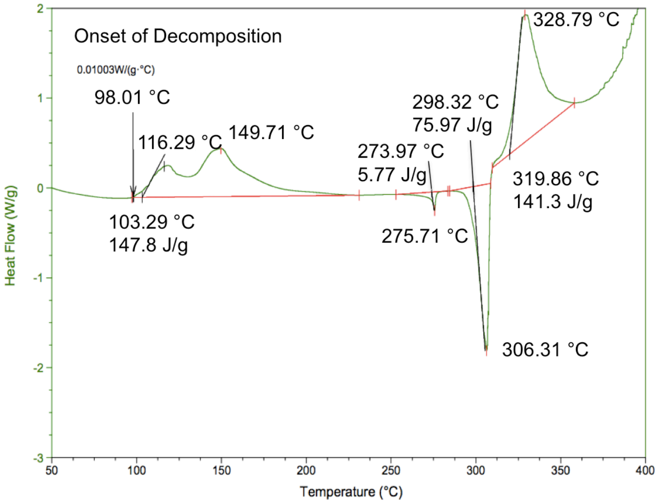

Figure 2. Early onset of exotherm in glove/Swheat/16 M $HNO_3/NaNO_3$ mixtures.

Studies of a bismuth-lined glovebox glove with a range of concentration of nitric acid (1, 8, and 16 M) with Swheat kitty litter/$NaNO_3$ reveal no change in behavior at 1M concentration, and an exothermic reaction at lower temperatures of c.a. 105 and 100 °C when using higher acid concentrations of 8M and 16 M, respectively. Use of 16M nitric acid to generate the exotherm in Figure 2 is an extreme case used to demonstrate the ability to lower the decomposition temperature.

- ***Lead and bismuth contaminants***

Studies revealed the presence of lead introduced from lead liners in some drums, including Drum 68660, which may also provide a potential trigger mechanism. A literature review of the reactivity of lead and bismuth nitrates with organic materials reveals that these nitrate salts have been implemented as

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[29] J. L Long, C. J Smith, "*Unstable Material Formed by reacting leaded Glove Box Gloves with Nitric Acid*," RFP-2648, Rocky Flats Plant, The Dow Chemical Company, Golden, Colorado, 1977; T. C. Johnson and J. W. Lindsay, "*Flammability of Lead Dry Box Gloves*," RFP- 1354, Rocky Flats Plant, The Dow Chemical Company, Golden, Colorado, 1969.

[30] Mound accident in "*Serious Accidents USAEC* Issue No. 293; August 26, 1968."

[31] D. Christensen, D. Bowersox, B. McKerley, R. Nance, LA-11069, "*Wastes from Plutonium Conversion and Scrap Recovery Operations*."

sensitizers in dry blasting agent explosive mixtures, as oxidizers for energetic mixtures, and as effective nitrating agents for organic nitration reactions at low temperatures. As noted above, nitric acid-contaminated leaded gloves can form highly reactive mixtures.[29-31]

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 $Bi(NO_3)_3$] as sensitizers and oxidizers in energetic mixtures. For example, a European patent application claims a mixture comprised of 25-30 wt% of bismuth subnitrate, 5-10 wt% fuel, 20-50% of an initiator explosive, and 1-10 wt% of a sensitizer to be a lead-free non-toxic pyrotechnic mixture,[32] and in 2005, a US patent was assigned to Nesveda et al. for the use of basic nitrates of bismuth as oxidizing agents in explosive ignition mixtures for production of ammunition primers.[33] In 1977, Ray et al. were granted a US patent for the use of lead nitrate as a sensitizer for dry blasting agents comprised of ammonium nitrate and fuels.[34] Additionally, it is noteworthy that bismuth oxide nanoparticles have found extensive application as oxidizers in nanoenergetic material formulations with aluminum fuels.[35] Preparation methods for these Bi_2O_3 nanoparticles have included the use of fuel/oxidizer mixtures of $Bi(NO_3)\cdot xH_2O$ and glycine.[36]

Since a number of nitrate salt waste drums may contain HNO_3 and lead from drum liners, it is worth some discussion of the 1997 study by Mishra et al. at the Colorado School of Mines (CSM) on the formation of explosive mixtures in nitric-acid-contaminated leaded glovebox gloves.[37] The work supported evaluation of the hazardous characteristics of residues found at the DOE's Rocky Flat Environmental Technology Site (RFETS). The CSM team found that treating Neoprene-Pb_3O_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 HNO_3, we initiated experiments aimed at assessing the potential for the lead and $Pb(NO_3)_2$ to exhibit exothermic reaction or chemical sensitivity.

Studies of solid lead flake and nitric acid with Swheat kitty litter/$NaNO_3$ reveal an exothermic reaction at the lower temperature of 110-120 °C. The lead nitrate shows very similar behavior to the bismuth-lined glovebox glove reactivity described earlier (Figure 2). 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.

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[32] G. C. Mei, J. W. Pickett, "*Lead-free non toxic explosive mix.*" Eur. Pat. Appl. 1443034A2, January 28, 2004.

[33] J. Nesveda, S. Brandejs, K. Jirasek, "*Non-toxic and Non-Corrosive Ignition Mixture*." US6964287B1, November 15, 2005.

[34] B. N. Ray, D. N. Bhattacharyya, "*Dry Blasting Agents*." US4039361, August 2, 1977.

[35] K. S. Martirosyan, L. Wang, A. Vicent, D. Luss, "Synthesis and performance of bismuth trioxide nanoparticles for high energy gas generator use." Nanotechnology, 2009, 20, 405609.

[36] K. S. Martirosyan, L. Wang, A. Vicent, D. Luss, "Synthesis and performance of bismuth trioxide nanoparticles for high energy gas generator use". *Nanotechnology*, 2009, *20*, 405609

[37] (a) B. Mishra, A. G. Raraz, D. L. Olson, W. A. Averill, "Formation of explosive compounds in acid-contaminated leaded rubber gloves Part II: Experimental verification", *J. Hazardous Mater.*, 1998, 57(1), 13-28. (b) B. Mishra, A. G. Raraz, D. L. Olson, W. A. Averill, "Formation of explosive compounds in acid-contaminated leaded rubber gloves Part I: theoretical analysis", *J. Hazardous Mater.*, 1997; 56(1), 107-116.

- ***Other metal impurities***

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, see Table 1) and lead from lead drum liners used in some drums, including the parent of Drum 68660. Complex mixtures of metal ions can display a combination of the behaviors of the individual components or can show behavior that is due to synergistic interactions among the different constituents.[16] 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 for comparison with Veazey et al.[2] The goal is to have a representative metal nitrate salt –Swheat mixture run by DSC, and then use the DSC kinetics to improve the fidelity of the model for drum 68660. Table 4 shows an example of a Stream Analyzer composition.

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. Initial studies of nitrate salt mixtures (Table 4) have shown that the mixtures are unstable, decomposing to gaseous products under ambient conditions, generating NO_x and leading to nitration of the organic Swheat material (at a 6 - 7% nitration level – mass % of nitrogen, see *Studies of Surrogate Salt Mixtures* below).

Table 4. *Stream Analyzer* Analysis of potential metal and oxalate salt concentrations for 68660.

Compound	Mass	Percentage
$Al(NO_3)_3 \cdot 9H_2O$	3.006	0.02378
$Ca(NO_3)_2 \cdot 4H_2O$	11.972	0.09473
$K(NO_3)$	2.623	0.02076
$Cr(NO_3)_3 \cdot 9H_2O$	0.157	0.00125
$Fe(NO_3)_3 \cdot 9H_2O$	8.160	0.06456
Salt-saturated liquid	0.245	0.00194
$Mg(NO_3)_2 \cdot 6H_2O$	78.764	0.62319
HNO_3	1.939	0.01534
$NaNO_3$	17.273	0.13666
NaF	0.231	0.00183
$Ni(NO_3)_2 \cdot 6H_2O$	0.078	0.00061
$Pb(NO_3)_2$	0.011	0.00009
$(COOH)_2$	1.930	0.01527
Total	126.39	1

- ***Nitration of organics***

We considered the potential for nitration (creation of material with a greater penchant for reactivity) or decomposition of organic material facilitated by metal impurities including iron, magnesium and aluminum from evaporator bottoms, lead from lead-liners used in parent drums, and a mixture of bismuth, tungsten, and lanthanum from glovebox gloves.

The key step in nitration of organics by nitric acid involves the generation of the nitronium ion, $[NO_2]^+$, a potent electrophile, from concentrated nitric acid.[38,39] Reaction of $[NO_2]^+$ with electrons in multiple bonds on the organic substrate leads to product formation ($R\text{-}NO_2$). Reaction of the nitronium ion with a hydroxyl group will give the nitrate ester ($R\text{-}ONO_2$).

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 and when considering the possible environmental conditions (e.g. low pH, metal ions, etc.), resulting in the possibility of more flammable materials (nitrated Swheat).

Studies of Surrogate Salt Mixtures

As described above, chemistry modeling codes (*Stream Analyzer*) were used to simulate the original evaporator process and generate an expected composition of nitrate salts as a model for contents of drum 68660. Current experimental efforts are now focused on the potential for synergistic effects of the combined metal nitrate salts predicted from these models, and to use this composition as a surrogate for a full-scale drum test to simulate 68660. For these studies, we turned to more sophisticated measurements of chemical energy release.

When energy is generated by a thermally induced chemical reaction and the heat transfer to the outside is lower than the heat generated, runaway reactions can occur. 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 automatic pressure tracking adiabatic calorimeter (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.

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[38] J. G. Hoggett, R. B. Moodie, J. R. Panton And K. Schofield, *Nitration and Aromatic Reactivity.* Cambridge University Press, Cambridge, UK, 1971

[39] C. K. Ingold, E. D. Hughes and R. I. Reed, *J. Chem. Soc.,* 1950, 2400-40

A thermal runaway reaction is usually investigated with a Heat-Wait-Search mode (HWS). The temperature of reaction as well as the temperature and pressure increase is measured. Additionally, the temperature and pressure increase rates can be determined. These are important values in order to characterize the worst-case scenario.

Starting with the Stream Analyzer models of the original evaporator process, a general mixed salt composition was generated (Sample WB-3 in Table 5). A series of surrogate RNS wastes were then created by mixing salts of varying composition with Swheat, HNO_3 and water to simulate the composition of RNS wastes (Table 5). Samples differed in the amount of iron, magnesium, moisture, etc. and the energetics of reaction were evaluated by APTAC. The series of mixtures studied to date demonstrate that iron is key to producing NO_2 from these surrogates, and that nitration of the Swheat kitty litter with NO_2 leads to the onset of a low temperature exotherm. At this time is unclear whether other metal ions assist in the Swheat nitration reaction. Lower amounts of water (waters of hydration of metal nitrate salts) seem to be associated with ease of nitration.

Table 5. Examples of surrogate RNS waste compositions for APTAC testing.

Compound	**WB-3**	**WB-4**	**WB-4-2**	**WB-Fe**	**PLA**
$Al(NO_3)_3 \cdot 9H_2O$	1.8	0.0	0.0	0.0	0.0
$Ca(NO_3)_2 \cdot 4H_2O$	7.2	8.4	9.7	9.2	7.5
$K(NO_3)$	1.6	0.0	0.0	0.0	0.0
$Cr(NO_3)_3 \cdot 9H_2O$	0.1	0.4	0.1	0.2	0.0
$Fe(NO_3)_3 \cdot 9H_2O$	4.8	5.7	6.7	0.0	4.5
H_2O	0.0	0.2	0.2	0.0	0.0
$Mg(NO_3)_2 \cdot 6H_2O$	47.0	20.6	23.9	22.5	41.3
HNO_3	0.8	0.0	0.0	0.0	0.8
$NaNO_3$	10.3	36.7	42.5	39.9	19.5
NaF	0.2	0.0	0.0	0.0	0.0
$Ni(NO_3)_2 \cdot 6H_2O$	0.1	0.0	0.0	0.0	0.0
$Pb(NO_3)_2$	0.1	1.9	2.2	2.1	0.0
$(COOH)_2$	1.1	1.4	1.6	1.5	1.5
Swheat	25.0	25.0	13.0	24.6	25.0

An example record from an APTAC experiment of a surrogate waste composition that shows evidence for a runaway reaction is shown in Figure 3 for surrogate sample WB-4. 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 planned full-scale testing, and give important insights in the nature of possible trigger mechanisms associated with metal ion impurities.

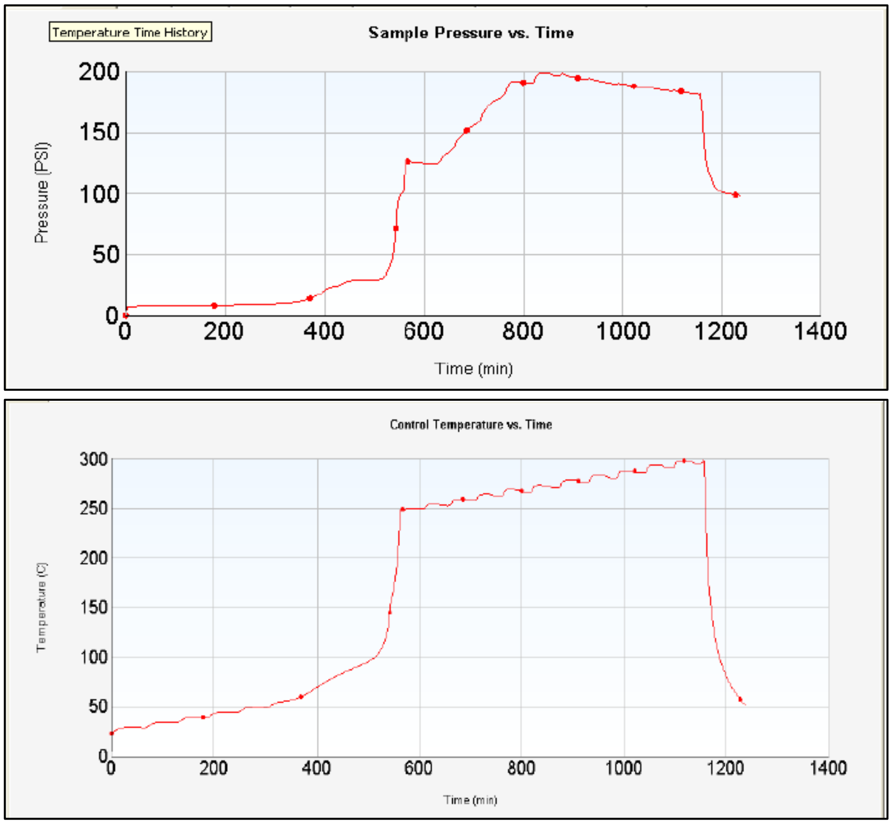

Figure 3. APTAC experimental run of an RNS surrogate test sample that provides evidence for thermal runaway reaction. Pressure evolution with time is shown in the top figure, and temperature evolution with time is shown in the bottom.

- ***Spontaneous self-heating and biological activity – ongoing work***

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.[40] 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. Experimental work is presently underway to evaluate the role that spontaneous self-heating due to biological processes may have played. 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.[41] If reaction rates

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[40] *DOE Handbook. Primer on Spontaneous Heating and Pyrophoricity*, DOE-DHBK-1081-94, December 1994

[41] Nolan, P.F. and J.A. Barton. "Some lessons from thermal-runaway incidents", *J. Hazardous Mater.*, 1987, 14, 233-239.

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 combustion may occur in piles of organic material containing high levels of moisture such as baled hay[42] and silo-stored grains[43] where heat is generated in the early stages by the respiration of bacteria, molds, and microorganisms —in some cases even after years of storage.[44] High moisture content is required for vigorous activity, and maintaining the moisture content below a predetermined level generally controls heating. Naturally occurring aerobic and anaerobic metabolic processes in microbes can generate heat at kW/m^3 levels if not adequately controlled.[45]

The self-heating of hay and compost piles is the result of a complex chain of events involving biological composting and chemical reactions.[46,47] In the first phase, a population of mesophilic, or moderate temperature bacteria and fungi raise the temperature to about 40 °C, which typically lasts for several days.[48] At this point their activities cease, and they are replaced by a mixed population of thermophilic (heat resistant) bacteria, actinomycetes, and heat-tolerant fungi that can last from a few days to several months depending on the size of the system and the chemical composition. The optimum temperature for these microorganisms is between 50 and 65 °C, and their activities terminate at 70–80 °C. After the thermophilic phase is completed, the temperature undergoes a gradual decline.[48,49] Proper conditions are necessary for optimal microbial growth, including the relative amounts of carbon and nitrogen, the balance between oxygen and moisture content, particle size, pH, and the physical size of the system that regulates heat loss.[48]

For hay bales, the temperature will generally rise to a peak and then decline over a 2 – 8 week period. If heat cannot dissipate, and reach temperatures above 70 °C, exothermic chemical reactions (oxidation) can occur leading to further increases in temperature and spontaneous combustion. There is danger of spontaneous combustion when internal bale temperatures reach 80 °C and this increases to near certainty by 100 °C.[46,47]

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[42] http://www.extension.umn.edu/agriculture/horse/nutrition/preventing-hay-fires, accessed 7/19/2014.

[43] U.S. Fire Administration, FEMA, Technical Report USFA-TR-096, *Special Report: The Hazards Associated with Agricultural Silo Fires*, April 1998.

[44] U.S. Fire Administration, FEMA, Technical Report USFA-TR-096, *Special Report: The Hazards Associated with Agricultural Silo Fires*, April 1998, page 6.

[45] See Figure 5.31 in *Biochemical Engineering Fundamentals*, by J.E. Bailey and D.F. Ollis, Second Edition, McGraw-Hill Book Company, New York, 1986.

[46] Mickan, F. Agnote AG1356, Haystack fires (spontaneous combustion), Published: October 2008, Farm Services Victoria/Dairy, Ellinbank Australia

[47] Sheaffer, C.C. and N.P. Martin. 1979. Hay Preservation. Agricultural Extension Service, University of Minnesota, Extension Folder Volume 489-1979.

[48] Cornell Waste Management Institute, Cornell University, “The Science of Composting” http://cwmi.css.cornell.edu/chapter1.pdf; see also Washington State University, Whatcom County Extension website, http://whatcom.wsu.edu/ag/compost/fundamentals/index.htm.

[49] Kutzner, H. J. (2000) Microbiology of Composting, in Biotechnology: Environmental Processes III, Volume 11c, Second Edition, (Eds H.-J. Rehm, G. Reed, A. Pühler and P. Stadler), Wiley-VCH Verlag GmbH, Weinheim, Germany. doi: 10.1002/9783527620968.ch2.

Most hay baled at moisture contents above 15% will experience some heating in the first 2 - 3 weeks after baling.[46] This heating is due to very low rates of plant respiration and enzyme and microbial activity by molds, yeasts and aerobic bacteria. Eventually the hay will reach its own equilibrium moisture content of approximately 15% moisture depending on climate. This increased heat and moisture further increases microbial activity resulting in ever increasing heat and more moisture. This moisture migrates by capillary or wicking action into surrounding drier material to begin the process anew in that area. However, at any stage during this heating process the heating may decline without reaching critical levels.

High moisture contents of > 15% in wheat/wheat by-products (Swheat composition) can lead to heat generation and spontaneous combustion just like the process that occurs with other hay or grain products.[50] The first stage is generally the observation of molding and clumping of the absorbent. This is followed by the combustion stage. The effects of acidity or nitrate salts on the potential for spontaneous combustion or fermentation, while not known in this case, may not completely prevent such processes from occurring. High acid and salt are expected to denature enzymes and destroy most biologics; however, the high inhomogeneity of the absorbent mixture coupled with neutralization of the nitric acid to near neutrality (pH 5 – 7) may prevent or modify enzymatic denaturation or potential deleterious affects on any endogenous microbes and yeast.

The inhomogeneity of the Swheat absorbent, water, and nitrate salts in the daughter drum 68660 makes these systems difficult to reproduce in a laboratory; however, the ratio of absorbent to water (free liquid) has typically been around 2:1 (˜33% water) or 3:1 (˜25% water) putting the water content above the 15% water content that is considered to be 'safe' for wheat based materials in anaerobic environments.

As noted previously, experimental work to evaluate biological activity is being conducted in support of this investigation. Pending completion of this experimental work it is plausible to consider that some level of biological activity could be taking place inside the kitty litter/$NaNO_3$ mixture and this biological activity could contribute to self-heating of the waste. At temperatures approaching freezing and below, any such biological activity in the waste would be significantly reduced preventing biological self-heating to occur.[49,57]

3.0 KEY FINDINGS

Several key findings were identified from the literature review and the extensive set of chemical reactivity studies and modeling efforts. These findings should be used as a basis for decisions regarding the disposition or treatment of the remediated nitrate salt wastes both at LANL and WCS, including

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[50] We note that large quantities of organic material are typically required (e.g. large hay bale rolls) to generate spontaneous combustion. While one might expect that spontaneous combustion would not be expected for damp Swheat in a 55 gallon drum, the insulating properties of the mixture and fiberboard liner make this a plausible scenario.

LANL's future efforts towards a small subset of drums with similar chemical characteristics, and the ultimate fate of the materials currently stored in Panel 7 at WIPP.

- ***The nitrate salt/Swheat 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 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. These findings are similar to thermal analysis of a variety of organic wastes (oxalate, citrate, EDTA, etc.), with nitrate salts reported previously for safety studies of Hanford Tank wastes.[16] Those studies indicated that similarly high temperatures (150 - 350 °C) were required to initiate reactions in the simple nitrate salt/organic mixtures of that study.[16,51] In our studies, simple nitrate salt/Swheat organic kitty litter mixtures were unreactive to electrostatic discharge (ESD) friction, or impact test procedures typically used to test the safety of energetic materials. Given the insulating nature of the nitrate salt/Swheat mixture, time-dependent chemical changes causing a basal increase in temperature leading to runaway chemical reactions have not been fully ruled out. Evaluation of Drum 68660 characteristics coupled with extensive chemical testing indicate that, in addition to the nitrate salt/Swheat organic kitty litter mixture, an additional trigger mechanism (or mechanisms) is likely required to raise the internal drum temperature high enough to initiate the nitrate salt/Swheat organic kitty litter mixture.

- ***An additional trigger mechanism is likely required to initiate chemical reactions needed to breach a drum***

The team of LANL chemists have demonstrated that the temperatures needed to initiate chemical reactivity may be substantially lowered when a combination of conditions exist. The teams 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 the potential for biological self-heating that could lead to chemical reactivity at substantially lower temperatures.

In the search for potential trigger mechanisms, it was determined that mixtures of metal nitrate salts with $HTEA(NO_3)$ (TEAN) do not result in exothermic behavior below 220 °C. It was also determined that complex mixtures of metal ions, particularly iron and magnesium, can generate NO_2 that facilitates the nitration of Swheat. ***These complex salt mixtures produce exothermic behavior as low as 60 °C.***[51] While encouraging for understanding factors that may lead to the breach of a drum, it is still important

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[51] We note that complex salt mixtures can generate low temperature (60 °C) thermal onsets similar to that reported in: R. D. Scheele, B. K. McNamara, L. M. Bagaasen, S. J. Bos, P. K. Berry, "Evaluation of Exothermic Reactions from Bulk- Vitrification Melter Feeds Containing Cellulose," Pacific Northwest National Laboratory, PNNL-16677 (2007)."

to understand how the drum can 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.[52]

Spontaneous self-heating generated by the respiration of bacteria, molds, and microorganisms is potentially important in the early stages and may be sufficient to raise the temperature to a level at which other exothermic chemical reactions can take place. Neutralization of free liquids, and sorption onto Swheat establishes conditions (moisture with near-neutral pH) that are expected to support the growth of natural biological activity. The potential for natural biological activity within Swheat kitty litter that may lead to self-heating are currently under study.

Our current working hypothesis and event description is as follows: 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 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.

From the combined results of literature studies, modeling, and experiments amassed to date, one can arrive at a plausible scenario in which heating from initial neutralization and/or mixing with Swheat,[53] low-level chemical reactions or natural biological self-heating, residual nitric acid, nitrate salts, glovebox gloves and/or lead/iron/magnesium nitrates that, when combined with the Swheat kitty litter, generated a series of exothermic reactions that heated and pressurized the drum, ultimately venting high-temperature gases and radioactive particles into the room. The exhaust gases are expected to be hot enough (1600 °C) to ignite when they contact air.[54] A notional ladder of exothermic reactions, leading to the possibility of bulk reaction of nitrate salts with the Swheat absorbent that was added during the remediation process at the LANL WCRR facility, is shown in Figure 4.

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 absorbent is the common ingredient in all reactions depicted in Figure 4, so that even if an external heat source was present, the commingling of Swheat (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 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.

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[52] Non-reacting drums in WIPP in the weeks leading up to the event are estimated to have risen from 10 °C to about 25 °C, and long-term temperatures would not exceed 30 °C, the temperature of the host rock at the depth of the repository: P. Stauffer, A. Jordan, and B. Robinson, "Temperatures Experienced by Nitrate Salt Waste Drums After Disposal in Panel 7," LANL Internal report (2014).

[53] Simple mixing of Swheat with water leads to a temperature increase of the mixture to 40 °C, which could have contributed to increased microbial growth rates as well as the initiation of chemical reactions. Bob Wingo, unpublished results.

[54] The products of combustion are not expected to be fully oxidized (using estimates from the thermochemical code Cheetah) leading to a gas that has large mole fractions of H_2, CO, and CH_4, which would further react when mixed with the air in Panel 7.

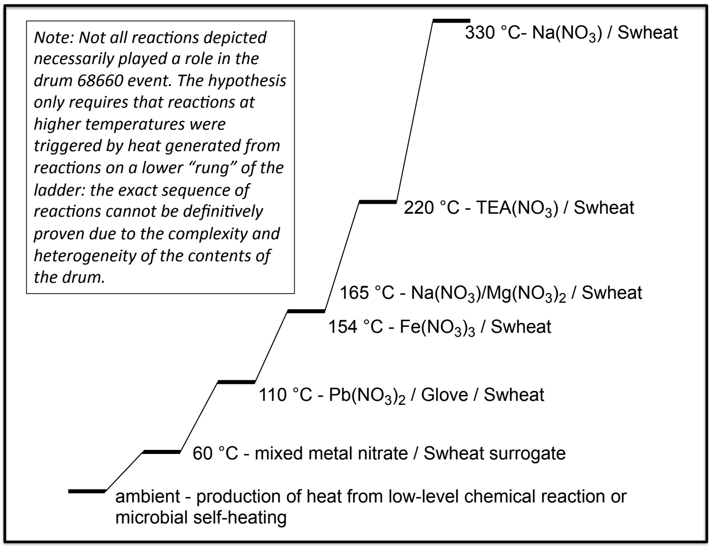

Figure 4. Notional ladder of stepwise biological or chemical reactions that may increase the temperature inside a drum.

4.0 DISPOSITION STRATEGY

Reaction chemistry efforts have uncovered a number of exothermic reactions with mixed metal nitrate salts and Swheat organic kitty litter that may serve as triggers for a series of step-wise reactions, raising the drum temperature and potentially causing the release observed in drum 68660. These reactions start with low-level chemical reactions and/or biological activity (self-heating, ca 60 °C), iron/magnesium (60 °C), lead (110 °C), iron (154 °C), sodium/magnesium (165 °C), TEA(NO_3) (220 °C) and ultimately the $NaNO_3$ (330 °C) as indicated in Figure 4. The proposed disposition strategy is intended to inhibit all of these step-wise reactions thus significantly reducing the likelihood of another WIPP like event.

4.1 Rendering Drums Safe From Further Reaction

A Container Isolation Plan for RNS waste at LANL was implemented to place the waste in a safe configuration, pending development and implementation of a plan to treat the waste and transport it to WIPP for permanent disposal. The measures in place to ensure the safety of the waste during storage include nesting the drums within Standard Waste Boxes (SWBs) to provide an extra layer of protection, placing the waste within a facility with HEPA filtration and active fire protection, and frequent visual inspections and monitoring of temperature and headspace gases to detect incipient exothermic reactions.

While the LANL waste in its current configuration is safe, the long-term solution is to render it unreactive. To do so, some of these controls will need to be removed in order to handle and treat the waste (e.g. denesting, opening of drums, etc.). This subsection summarizes the methods that were considered to enable safe handling of the RNS waste outside of the engineered controls listed above, and the next subsection discusses treatment options. Recommendations are made based on the knowledge gained from the scientific studies developed herein.

4.1.1 Water Addition

All of the chemical reactions identified in our studies can be shut down or inhibited by the addition of water, so long as water addition does not result in other chemical or biological reactions giving rise to unintended consequences. Our experiments show that water addition to surrogates results in substantial cooling due to endothermic dissolution of nitrate salts. This can initially cool surrogate samples to the freezing point of water. This initial cooling effect is highly desirable in quenching or slowing chemical reactivity (see 4.1.2). Hence, under off-normal conditions (e.g., fire suppression system actuation), water addition would function as an effective safing mechanism.

However, there are risks associated with water addition. The addition of water will generate nitric acid associated with nitrate salts and enhance the decomposition of the organic Swheat kitty litter. Our experiments show that with time, the Swheat/nitrate salt surrogate materials decomposed after water addition, generating significant gas evolution (Figure 5, left), and in some cases expulsion (or burping) of contents from sealed sample containers (Figure 5, far right). In addition, discussion with the manufacturer of Swheat indicates that Swheat has a significant natural microbial content and will undergo aerobic fermentation with the addition of water producing ethanol, carbohydrates, and other fermentation products.

Figure 5. (left) A 3:1 (volume to volume) Swheat to nitrate salt simulant ratio containing oxalate, that was 'quenched' using tap water at a 1:1 (mass to mass) ratio based on mass of Swheat in sample. There is clear bubble formation as evidence of gas generation on the surface of the sample. (right) Sample S1-5 is a simulant sample prepared on 23 June 2014. A 3:1 (volume to volume) Swheat to nitrate salt simulant ratio, that was 'quenched' using tap water at a 1:1 (mass to mass) ratio based on mass of Swheat in sample. Sample sat relatively undisturbed since mid-July, albeit with occasional handling, but no evidence of pressurization or unusual visual characteristics. Approximately 50 days later, a Leak/burp was noticed on 12 August 2014.

4.1.2 Temperature Control

The rates of most chemical and biological reactions are sensitive exponential functions of temperature.[55,56] Chemical reaction rates increase with an increase in temperature because at higher temperature, a larger fraction of reactant molecules possesses energy in excess of the reaction energy barrier, allowing the reaction to proceed more readily. The influence of temperature on reaction rate is described by the Arrhenius equation with parameters *R* for the gas constant, *T* for the absolute temperature, *A* for the pre-exponential factor, and the activation energy E_a.

$$k = Ae^{-Ea/RT}$$

Reactions in solution have typical E_a values in the range of 10-30 kcal/mol. As the temperature increases, the rate of reaction also increases. These values corresponds to a rough approximation that reaction rates increase by a factor of 2 or 3 for every 10°C rise in temperature.[55]

One has to be careful not to take this too literally. It doesn't apply to all reactions. Even where it is approximately true, it may be that the rate doubles every 9°C or 12°C. The number of degrees needed to double the rate will also change gradually as the temperature increases. Increasing the temperature increases reaction rates because of the disproportionately large increase in the number of high-energy collisions. It is only these collisions (possessing *at least* the activation energy for the reaction) that result in a reaction. This makes temperature a powerful tool in controlling the rate of a chemical reaction (an exponential effect).

Temperature also has a powerful effect on biological reactivity. Most organisms grow very little or not at all at 0 ^{o}C.[57] Low temperatures are used in household refrigerators to control microbial growth. At low temperatures, microbial metabolism slows considerably, and the reproductive rate is reduced. However, at freezing temperatures and with active cooling, all bacterial growth is inhibited and reduced. Growth rates will be slow enough to preclude any increase in temperature from the endogenous bacterial organisms. Mesophilic bacteria have an optimum temperature range of 30 – 40 ^{o}C and if the temperature is kept near freezing with active cooling, these organisms, which are primarily responsible for increasing temperatures to ~40 ^{o}C from their growth, cannot grow and cause any additional temperature increase.[58]

Monitoring data indicate a qualitative correlation between CO_2 concentration and temperature, as evidenced by the measured daily high temperature measured for the SWB containing the daughter to 68660, drum 68685. Assuming that this correlation is causal rather than due to some other factor, these data suggest that temperature is influencing the chemical and/or biological activity in the drums being stored at LANL. Referring back to Figure 1, we note that from a peak of ~30,000 ppm CO_2 at daily peak temperatures near 25 ^{o}C in the summer, we are now seeing concentrations of ~10,000 ppm at daily peak temperatures near 12 ^{o}C, a nearly three-fold decrease in equilibrium concentration. Coarsely, if we

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[55] Connors, K. A. Chemical Kinetics, the Study of Reaction Rates in Solution, VCH Publishers, 1990.

[56] Palmisano, A. C.; Barlaz, M. A. *Microbiology of Solid Waste*, CRC Press, New York, 1996

[57] Peleg, Micha; Normand, Mark D.; Corradini, Maria G. *Critical Reviews in Food Science and Nutrition* (2012), 52(9), 830-851

[58] Bob Williams, LANL, unpublished work.

assume that the concentration is proportional to the rate of the production, the rate has decreased three-fold for an ~12 °C drop in temperature.

Finally, we note that established chemical industry guidelines maintain the normal process operating temperature more than 50 °C less than the ARC or APTAC-measured onset temperature for an exothermic reaction.[59] The lowest temperatures for exothermic onset that we have measured with mixed-metal salt mixtures and nitric acid is close to 60 °C. This indicates that cooling to 10 °C would provide a safe temperature margin, well below the temperature of the worst-case exothermic reactivity for workers to remove the drums from their current storage configuration in order to handle and process the waste.

4.1.3. SF_6 addition

Due to its excellent insulating and arc-suppression properties,[60] sulfur hexafluoride (SF_6) is widely used in gas-insulated switchgear. During a workshop with the DOE Technical Assessment Team, it was suggested that LANL examine the use of SF_6 as an approach to preventing chemical reactivity in the drums. This novel approach had a number of attractive features provided that the material would remain chemically inert under the conditions of the large number of chemical components of the drums. In arc-suppression applications, during a partial electrical discharge SF_6 decomposes into various by-products according to discharge scenarios. These by-products are often used to detect and identify partial discharge.

Previous literature suggests that in the presence of free radicals, SF_6 cannot be considered inert. We examined the DSC of $Na(NO_3)$/Swheat under an atmosphere of SF_6, and found enhanced chemical decomposition, with the onset of exothermic behavior near 152 °C. Further consideration of SF_6 for drum safing was abandoned.

4.1.4 Recommendations

Taken together, the above data argues against the use of water to render the drums safe and indicates that cooling should be considered as the primary safing method once drums are removed from their current storage configuration and the waste is handled. Lowering the temperature of the waste will reduce *both* chemical and biological activity and reduce the likelihood of exothermic chemical or biological reactions during subsequent disposition activities. Therefore, it is recommended that the waste temperature be reduced to -10°C or lower and this temperature maintained for a minimum of 2 days in order to reduce both chemical and biological activity. After this cold step, subsequent disposition activities can be performed with the waste temperature ≤ +10°C (50°F), a more practical temperature for handling the waste once the drum is opened. The latter temperature is 50 °C below the lowest exothermic reaction temperature observed in APTAC studies, consistent with safety recommendations from the Center for Chemical Process Safety,[59] and would also eliminate the potential for the growth of mesophilic bacteria.[58] A convenient method for cooling would be to move drums into a low temperature

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[59] Center for Chemical Process Safety "Guidelines for Chemical Reactivity Evaluation and Application to Process Design", AIChE, New York, NY, 1995

[60] Greenwood, N. N.; Earnshaw, A, Chemistry of the Elements, Second Edition, Butterworth Heinemann, Oxford, 2001.

walk-in freezer. Since the thermal conductivity of the Swheat/nitrate salt mixture is not known, experiments are being conducted to determine the time necessary to take a 55 gallon drum of RNS waste inside of an SWB to below -10 °C, and then warm it back to +10 °C.

4.2 Disposition of 'safed' Drums

It is necessary to remove water from Swheat to avoid self-heating due to biological activity. Hence the disposition method should provide for absorption and removal of water as Swheat undergoes decomposition. An inorganic medium that will continue to absorb water is recommended. This would include mixing the nitrate salts with inorganic absorbent to a threshold that avoids exothermic reaction. This leads to the use of grouts and natural mineral absorbents for disposition.

4.2.1 Grout

Cementation is one of the most commonly used methods for conditioning radioactive wastes.[61] It provides a cost-effective solution for encapsulation of various kinds of radioactive waste into a solid, safe form suitable for long-term storage. Cementation through the use of specially formulated grouts provides the means to immobilize radioactive material that is in solids and in various forms of sludges and precipitates/gels (flocks) or activated materials. In general the solid wastes are placed into containers. The grout is then added to the container and allowed to set. The container with the now monolithic block of concrete/waste is then suitable for storage and disposal. Water based grouts have the potential to dewater over time.

Cement-based materials are used worldwide to solidify and stabilize low- and intermediate-level radioactive wastes.[62] The use of grout is standard technology that has stabilized Resource Conservation and Recovery Act (RCRA) heavy metals, such as chromium, lead, and mercury, and produced solid waste forms that meet the U.S. Environmental Protection Agency requirements.[63] By immobilizing the waste and acting as a barrier around it, the cement-based material reduces the likelihood of radiological constituents being released from the waste and transported into the environment.

4.2.2 Natural mineral absorbents

Natural minerals that can act as adsorbents have high surface areas and pore spaces, which enables liquids to enter natural voids in the mineral. Diatomite, sepiolite and attapulgite have been used as industrial spillage adsorbents and for amending soil in agriculture.[64] These highly absorbent minerals can retain up to 60-70% of their weight in liquid. Zeolites are less absorbent, but they are highly *adsorbent*, based on the ability to preferentially capture and release ions. Bentonite is another mineral that has been growing in popularity as landfill, hazardous waste remediation, and cat litter due to its ability to absorb water, swell, and form a water-tight seal. Generally, softer minerals have higher

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[61] Onofrei, M.; Gray, M. N.; Coons, W. E.; Alcorn, S. R.; *Waste Management* (Cementitious Materials in Radioactive Waste Management) 12 (2-3), 1992, 133-154.

[62] International Atomic Energy Agency. TECDOC Series No.1397. Vienna, Austria, 2004.

[63] National Research Council, "The State of Development of Waste Forms for Mixed Wastes." Washington, DC: National Academy Press. 1999.

[64] Crossley, P. *Industrial Minerals*, May 2002, 34

absorbent capacities, but are accompanied with greater tendency to produce dust. One of the largest volume applications for absorbent minerals such as bentonite, montmorillonite, attapulgite, speiolite and diatomite is in pet litter.[65]

Zeolites. Zeolite refers to a group of minerals comprised of hydrated aluminosilicate cages in which the water is held in cavities in the lattice.[66,67,68] Zeolites have large vacant spaces or cages in their structures that allow large cations like sodium, potassium, and calcium, and relatively large molecules such as water and ammonia, or large oxo ions like carbonate and nitrate to become sequestered in the lattice. The lattices are negatively charged and they loosely hold cations such as calcium, sodium, ammonium, and potassium as well as water. Their ability to exchange one cation for another is known as their "cation-exchange capacity" or "CEC". Cation-exchange capacity is a measure of the number of cations per unit weight available for exchange, usually expressed as milliequivalents per 100 grams of material. An example of a zeolite structure illustrating the channel structure for water and ion absorption can be seen in the structure of the natural mineral mordenite, shown in Figure 6.

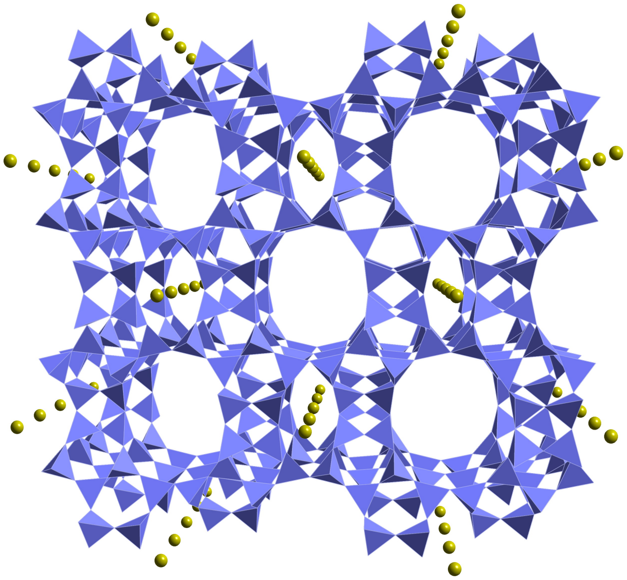

Figure 6. An illustration of the natural zeolite mineral mordenite ($NaAlSi_5O_{12}•3H_2O$), showing a polyhedral representation of a ringed aluminosilicate framework, looking down the c axis and highlighting channels for uptake of water or other ions. The green atoms are sodium ions of the structure.

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[65] Moore, P. *Industrial Minerals*, December 2000, 61

[66] Virta, R. L., U.S. Geological Survey Minerals Yearbook, 2000, 85. http://minerals.usgs.gov/minerals/pubs/commodity/zeolites/zeomyb00.pdf

[67] Virta, R. L., U.S. Geological Survey-Minerals Information, 1997. http://minerals.usgs.gov/minerals/pubs/commodity/zeolites/zeomyb97.pdf

[68] Mumpton, F. A. *Proc. Natl. Acad. Sci.* 96, 1999, 3463-3470

Natural zeolites in the US are commercially mined from deposits in the Western states (AZ, CA, ID, NV, NM, OR, TX). The most commonly mined zeolites include chabazite, clinoptilolite, and mordenite.[69]

Finally, we note that thermal decomposition of metal nitrate salts can produce gaseous NO_2 as noted above.[70] Gas phase reaction of NO_2 and N_2O_4 with various organic molecules over metal oxide,[71] zeolite,[72] or montmorillonite catalysts has been shown to nitrate organic molecules at high temperature (> 150 °C), which could have implications for the remediation strategy proposed below.[73,74] However, in addition to the extreme conditions required (highly improbable in reprocessed drums) zeolite catalysts are prone to rapid catalyst deactivation,[74] eliminating this as a potential concern for the reprocessed material.

4.2.3 Recommendation for Remediation

Based on the discussion of biological activity in Swheat materials, it is important to avoid the addition of water for safing the drums. Similarly, we recommend avoiding the addition of water for remediation. As a result, the addition of a natural mineral adsorbent is preferred over grout because cementation involves addition of water at some time during processing. Of the natural minerals available, we recommend a common zeolite such as clinoptilolite, widely available throughout the Western US. If for some reason, natural zeolites are found to be unsuitable, then grout is a reasonable alternative with the important caveat that a drum should never be allowed to sit for more than 30 days once water has been added. As noted previously, cement-based materials are used worldwide to solidify and stabilize low- and intermediate-level radioactive wastes,[62] our recommendations with respect to water addition and cementation apply only to the unique RNS waste materials being discussed herein. The RNS salts mixed with zeolite will need to be studied to establish the concentration at which the most reactive mixture of RNS wastes become a non-oxidizer when mixed with either zeolite or grout, analogous to the original EMRTC study with nitrate salts.[6]

5.0 QUALITY ASSURANCE

5.1 Conduct of Research and Development

The research, development and testing performed in support of this report was conducted in a variety of facilities spanning basic/applied research and development, radiological research and development, and weapon research and development facilities. The *Los Alamos National Laboratory Quality Assurance Program* (SD330) utilizes a graded approach to quality assurance based on the type of work and facility where the work is conducted. The work in support of this report was conducted according to

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[69] Zeolites (natural), USGS Mineral Commodity Summaries 2011

[70] B. V. L'vov, A. V. Novichikhin, "Mechanism of thermal decomposition of anhydrous metal nitrates", *Spectrochim. Acta B*, 1995, 50, 1427.

[71] H. Sato, K. Nagai, H Yoshioka, Y. Nagaoka, *Appl. Catal. A*. 1999, 180, 359

[72] L. V. Malysheva, E. A. Paukshtis, K. G. Ione, *Catal. Rev. – Sci. Eng*. 1995, 37(2), 179.

[73] (a) Wang, Shue Cieh Paul *Eur. Pat. Appl*. (1986), EP 174600 A1 1986031. (b) Wang, Shu Chieh P.; Sherwin, Martin B., U.S. (1985), *US 4517392 A 19850514*. Ni, Ping; Li, Shen-wei, *Guangzhou Huagong* (2010), 38(8), 94-95.

[74] M. G. Kuba, R. Prins, G. D. Pirngruber, *Applied Catalysis A: General* 2007, 333, 78.

SD601, *Conduct of Research and Development* in order to increase the stock of knowledge, and to use that knowledge to devise new information, data, or proof of concept leading to an understanding of the reactive chemistry associated with MIN02 wastes and WIPP drum 68660.

This approach has generated an understanding of the chemical and biological processes that may have led to the breach of drum 68660, which has allowed the R&D teams to eliminate many unproductive hypotheses and focus on a productive subset for more detailed analyses. This approach has provided a basic understanding the reactive chemistry associated with the MIN02 wastes, and generated a set of recommendations for safing and remediation. Because those recommendations will affect *Safety Basis* decisions, the Laboratory will reproduce and refine the subset of important experiments that support safety basis decisions under a more rigorous Quality Assurance Test Plan according the SD330, attachment B1, *Nonreactor Nuclear Facilities and Radiological Facilities QA Requirements.*

6.0 APPENDICES

Appendix 1. Gas analysis of the subset of 7 SWBs exhibiting highest concentrations of CO_2 and N_2O.

Appendix 2. Experimental test matrix developed to investigate the various chemicals introduced by process changes related to the remediation of nitrate salt wastes.

Appendix 3. Chemical analyses performed on empty parent drums that contained unremediated nitrate salts.

Appendix 1

Summary of LANL Nitrate Salt Bearing Waste Container Headspace Gas Characterization Activities.

Headspace gas analysis was performed on 25 drums containing nitrate salts beginning, May 7 thru May 12, 2014 as part of an initial investigation of this waste stream. These analyses were performed to see if observed gas concentrations could be attributed to decomposition of waste from interaction with the radioactive content of the drums. Radiolytic processes produce simple gas molecules from the interaction of radiation with organic and inorganic material in TRU waste. Hydrogen is typically the principal gas produced from the interaction of radiation with organic. During headspace analysis for hydrogen, levels of other gases including CO, CO_2, and N_2O are also measured. Gaseous CO_2 can also be formed from radiolysis, and its concentration depends on the specific composition of the waste. From experiments that studied the radiolysis of selected TRU waste surrogates, the relative amount of CO_2 and H_2 that is produced has been established under a range of conditions. From these investigations, the ratio of the amount of CO_2 to H_2 produced was greatest for poly vinyl chloride, with a maximum ratio for this material to be 6.5 CO_2/H_2. Other waste types did not produce as much CO_2 and therefore this ratio would be less than 6.5.

The analysis of the 25 nitrate salt drums initially selected revealed that some drums had CO_2 to H_2 ratios of >100. This suggests that gas generation in some cases cannot be attributed solely to radiolysis of the TRU waste. This supposition is reinforced by the observation of nitrous oxide > 1,000 ppmv, which would likely be indicative of nitrate salt reaction chemistry. Atmospheric concentrations for these gases are approximately 450 ppmv and 350 ppbv respectively.

LANL began characterizing the headspace gas of 55 standard waste boxes (SWB) containing remediated and un-remediated nitrate salt waste for Volatile Organic Compounds (VOCs) by Gas Chromatography/Mass Spectrometry (GC-MS) and for permanent gases using GC with a Thermal Conductivity Detector (GC-TCD). Permanent gases are those that remain gaseous at standard temperature and pressure. Daily monitoring of a subset of these 55 SWBs was initiated on May 19, 2014. Resource limitations required that daily sampling be discontinued on boxes with low gas concentrations so sampling of the other SWBs could be performed. All 55 SWBs have now been characterized. Elevated concentrations of CO_2 and N_2O have been observed at concentrations well above normal atmospheric concentrations in some of these 55 SWBs (Attachment 1). These concentrations cannot be explained based on radiolysis of waste drum content 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 degradation. N_2O is believed to result from the oxidation of material contained within the nitrate salt containing waste. The N_2O concentrations observed, ranging from (100 – 9000 ppmv), are above the normal atmospheric concentration of ~ 350 ppbv. Gas analysis of the subset of 9 SWBs exhibiting highest concentrations of CO_2 and N_2O are summarized in attachments.

While high CO_2 concentrations are expected to be proportional to the magnitude of chemical reactivity taking place in any given drum, they are not, on their own, and indicator that a drum enter a thermal runaway process. Trending, however, can be used to determine if the chemical reactivity is steady or accelerating over time. Thus, over time, we would expect to see changes in headspace concentrations that would increase, as the temperature and magnitude of reaction chemistry increases in the drum. Since we have not seen any drums with any significant increases in CO_2 concentration with time we suggest less frequent sampling (we note that this also supports minimizing worker risk –minimizing the time near the drums is a best practice). We will continue to monitor the trend, and if we see increased activity, we would establish more frequent temperature and head space monitoring.

As part of our initial investigations, we performed solid phase microextraction (SPME) analyses beyond the requirement to monitor for organic compounds which may exceed their individual flammability limits. The detection limits for organic compounds without SPME is sufficient to establish that concentrations of organic vapors do not approach flammability limits. SPME was performed for the purpose of detecting organic molecules which could be an ignition initiator at very low concentrations. No compounds have been observed which could undergo auto-ignition and therefore no initiator has been identified.

Ongoing analyses are focused on the monitoring of hydrogen gas concentrations since the LFL for hydrogen is established, readily measured and actionable levels can be established. The concentrations of oxidation products (eg: CO_2 and N_2O) is ancillary to the hydrogen gas concentration measurement, but provides considerable additional insight into the extent of chemical reaction in the nitrate salt bearing weight stream. While no action level based in $[CO_2]$ and $[N_2O]$ is yet established, a rapid change in the concentration of these gases may suggest more careful temperature monitoring to detect the potential for thermal runaway.

Remediated Nitrate Salt Container Headspace Gas Analysis

	68685				69553				69615				69616				SB50069				SB50452				SB50522			
Date	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm
05/19/14	54		1772																									
05/20/14	62		2282																									
05/21/14	80		3171																									
05/22/14	87		3677																									
05/23/14	65		3609																									
05/24/14	127		6314																									
05/25/14	97		6302																									
05/26/14	126		7180																									
05/27/14	143		8300																									
05/28/14	138		8263																									
05/29/14	123		8506																									
05/30/14	147		8909																									
05/31/14	107		10230																									
06/01/14	125		8278																									
06/02/14	145		10639																									
06/03/14	146		10506																									
06/04/14	115		11863																									
06/05/14	143		12754																									
06/06/14	112		12955																									
06/07/14	121		13962																									
06/08/14	111		12602																									
06/09/14	114		13219																									
06/10/14	69		9287																									
06/11/14	131		17089																									
06/12/14	57		7904																									
06/13/14	114		15887																									
06/14/14	74		11701																									
06/15/14	99		14963																									
06/16/14	121	769	16498	5110																								
06/17/14	112	691	15969	5117																								
06/18/14	64	713	12334	3804																								
06/19/14	119	964	20237	6591																								
06/20/14	35	443	9853	3255																								
06/21/14	114	830	18847	6009																								
06/22/14	133	1091	20304	6477																								
06/23/14	100	788	15999	5059																								
06/24/14	71	565	12856	4010																								
06/25/14	142	1057	22667	7203																								
06/26/14	92	852	18877	6016																								
06/27/14	104	818	17714	5517																								
06/28/14	69	693	15710	4886																								
06/29/14	136	1175	23205	7394																								
06/30/14	81	849	18787	5966																								
07/01/14	126	1063	22982	7231																								
07/02/14	56	757	14828	4619																								
07/03/14	122	1100	22978	7167																								
07/04/14	61	680	16019	4982																								
07/05/14	106	949	20298	6295																								
07/06/14	107	974	21555	6771																								
07/07/14	115	1096	23660	7412																								
07/08/14	107	1072	22584	7119																								

Remediated Nitrate Salt Container Headspace Gas Analysis

	68685				69553				69615				69616				SB50069				SB50452				SB50522			
Date	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm
07/09/14	106	1123	24984	7819																								
07/10/14	107	1172	25711	7990																								
07/11/14	119	1165	24560	7600																								
07/12/14	113	1127	26119	8302																								
07/13/14	84	963	20897	6452																								
07/14/14	64	788	18083	5541																								
07/15/14	105	1245	27856	8669																								
07/16/14	63	762	19271	5946																								
07/17/14	99	1055	23037	7118													799	1719	40330	7297								
07/18/14	118	1193	26921	8391													790	1752	40331	7402								
07/19/14	91	978	21197	6608													821	1717	40114	7231								
07/20/14	55	925	21770	6716													768	1765	40967	7495								
07/21/14	121	1262	28155	8784													776	1657	38707	7034								
07/22/14	110	1224	28656	8854													795	1724	40159	7193								
07/23/14	111	1160	26284	8206													794	1686	40188	7244								
07/24/14	108	1264	26414	8230									115	918	27870	6152	891	1810	41238	7433	551	1069	25183	5196	21975	539	62032	945
07/25/14	109	1091	26541	8212									268	1617	45757	10363	835	1758	41207	7454	439	1149	27142	5630	26838	662	69674	993
07/26/14	89	991	23888	7444									126	1098	33518	7547	713	1547	36694	6643	486	1014	23931	5001	20998	537	61790	971
07/27/14	115	1301	29375	9226									165	1229	35267	7962	809	1716	39981	7234	296	895	22385	4603	27179	639	72050	1134
07/28/14	111	1186	26734	8372									185	1396	40753	9194	831	1694	41282	7502	578	1113	26505	5555	24154	630	68024	1011
07/29/14	119	1257	27797	8642									239	1618	43649	9892	547	1607	38496	6963	359	1017	24723	5128	28020	684	76858	1155
07/30/14	108	1214	27628	8637									171	1406	40257	9120	727	1720	40217	7274	480	1093	25154	5320	23282	626	69258	1086
07/31/14	107	1155	26177	8194	214	909	31097	4517																	23961	525	66745	982
08/01/14	110	1321	27978	8623	160	637	24522	3564																	21551	509	67320	1068
08/02/14	78	1283	27404	8426	210	863	29498	4282																	20507	563	63031	989
08/03/14	119	1255	27718	8660	191	819	29686	4347																	16585	510	58759	916
08/04/14	116	1178	27441	8571	202	844	28601	4142																	19640	554	67041	1031
08/05/14	120	1174	27878	8691	196	833	31130	4539																	15630	522	62544	964
08/06/14	115	1236	28195	8867	168	707	27704	4077																	17687	476	64068	1036
08/07/14	102	1194	25590	8031					151	392	11857	485													13890	520	60111	920
08/08/14	101	1142	24599	7633					172	405	12777	506													16420	496	64567	1027
08/09/14	123	1404	28754	9018					141	369	11350	481													14813	573	64181	1032
08/10/14	134	1505	29935	8352					174	444	13317	558													14862	554	64810	991
08/11/14	128	1265	28751	9033					169	436	12708	548													12188	538	62173	1017
08/12/14	114	1183	27049	8514					157	358	12093	510													12624	507	65850	1028
08/13/14	87	927	21367	6749					96	263	8828	421													12071	472	63927	1104
08/14/14	116	1293	28165	8900	206	740	29180	4340	153	362	12342	557					720	1370	34540	6169					10291	439	56528	873
08/15/14	98	1058	22213	6941	166	784	26350	3902	108	236	8699	386					647	1437	33305	5908					12242	489	58382	976
08/16/14	110	1243	25159	7912	179	799	25790	3757	151	372	10826	489					758	1682	39200	6989					9258	455	59976	928
08/17/14	98	1092	23720	7590	205	946	29995	4439	72	194	6049	261					595	1333	31273	5554					11912	469	63588	1078
08/18/14	107	1121	26968	8612	219	939	32177	4833	162	480	13109	592					741	1775	41161	7389					9111	448	57532	918
08/19/14	131	1205	29004	9193	196	835	29942	4551	88	208	6983	353	311	1650	45119	10266	639	1657	40763	7335	677	1311	31626	6510	8549	419	54547	968
08/20/14	116	1258	28791	9130	154	616	23009	3448	142	452	12049	562	266	1536	42951	9801	569	1498	36150	6483	582	1181	28124	5833	9490	543	60061	1040
08/21/14	96	988	22811	7399	196	856	30029	4389	141	412	11782	544	282	1437	41706	9580	570	1386	35803	6314	624	1228	30314	6185	8971	460	59551	972
08/22/14	115	1050	25082	7937	146	636	21173	3105	128	399	10413	453	226	1236	36738	8301	623	1594	37026	6477	594	1121	26516	5457	7829	352	52471	829
08/23/14	120	1196	26589	8430	171	987	29584	4365	94	307	9007	407	266	1367	39895	9110	541	1442	35104	6190	634	1218	29331	6004	7816	456	58254	894
08/24/14	119	1225	26003	8258	131	602	19406	2810	122	420	11559	513	118	788	22677	5088	542	1331	34395	6049	639	1148	28632	5854	8081	443	57782	908
08/25/14	99	886	23361	7423	175	795	27973	4049	66	246	6986	362	264	1315	37969	8574	498	1301	32036	5664	639	1195	28881	5866	8300	394	55044	920
08/26/14	108	1078	24679	7765	133	544	20587	3069	121	384	10866	484	149	1125	34212	7789	522	1183	29958	5262	513	977	26195	5284	8713	400	56774	872
08/27/14																												
08/28/14	117	1261	25765	8184	176	814	29173	4303	42	161	5032	221	289	1605	41551	9423	499	1413	31439	5454	624	1208	29125	5949	9472	455	60365	967

Note: Yellow indicates greater than 1% hydrogen and red indicates greater than 2% hydrogen - the LEL is 4% hydrogen.

Remediated Nitrate Salt Container Headspace Gas Analysis

	68685				69553				69615				69616				SB50069				SB50452				SB50522			
Date	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm
08/29/14																												
08/30/14																												
08/31/14																												
09/01/14																												
09/02/14	96	1013	21716	6918	146	711	23055	3428	114	355	10853	535	246	1275	36423	8257	364	1048	25820	4435	548	1012	25803	5199	7373	362	53304	859
09/03/14	88	677	15348	4857																					6986	259	39338	633
09/04/14	126	1120	27887	8902	125	519	21770	3307	106	428	10414	511	235	1200	33958	7707	484	1391	33346	5801	499	1021	25752	5240	7911	500	57002	924
09/05/14	129	1172	25641	8192																					8823	407	55026	900
09/06/14	121	1145	25132	7982																					7588	425	55944	907
09/07/14	125	1165	25072	7951																					7841	343	52486	840
09/08/14	139	1191	27700	8839	87	429	15482	2288	95	352	8935	465	225	1245	35036	7885	529	1387	33835	5812	543	985	24810	4914	7930	460	54799	886
09/09/14	122	1061	25544	8121																					8771	427	62741	1082
09/10/14	132	1104	26452	8332																					8625	427	62596	1031
09/11/14	100	930	20830	6597	150	683	24156	3579	57	208	5595	251	261	1283	35802	8142	375	1055	25053	4295	565	997	24647	4958	7071	391	51431	822
09/12/14	134	1111	25732	8208																					8758	497	61598	1004
09/13/14	126	993	24294	7750																					7478	456	57344	961
09/14/14	114	1012	22444	7093																					8202	445	52319	849
09/15/14	87	813	20465	6530	148	735	23914	3539	101	405	9965	514	218	1252	34044	7636	430	1223	29994	5129	584	1124	27536	5474	6879	384	56055	928
09/16/14	135	1114	24857	7751																					8557	438	60782	947
09/17/14	119	1070	25989	8313																					7959	386	62978	1028
09/18/14	115	934	21898	6913	150	815	26660	3973	68	303	7511	392	235	1200	33958	7707	458	1318	31607	5358	612	1217	28950	5801	6473	416	57365	956
09/19/14	136	1139	24807	7831																					8601	496	62213	1036
09/20/14	127	1089	23460	7439																					7487	486	55543	925
09/21/14	123	1102	22597	7087																					7797	442	57549	943
09/22/14	71	627	15715	4880	138	590	22617	3347	55	214	5390	246	249	1162	31952	7150	348	1005	23096	3775	492	905	22883	4514	5902	443	52639	880
09/23/14	136	1112	24541	7906																					8169	518	61908	1068
09/24/14	142	1108	24877	7861																					7454	484	63321	1089
09/25/14	138	1077	24263	7677	167	765	25738	3853	106	373	9308	613	290	1241	33948	7591	513	1321	32458	5416	666	1046	28375	5659	7296	447	55893	946
09/26/14	111	901	19367	6019																					6621	446	53632	922
09/27/14	120	1101	21935	6810																					6503	363	50525	899
09/28/14	134	1154	22047	6932																					6966	465	53666	961
09/29/14	130	1096	23585	7428	143	696	21353	3154	101	340	8926	469	259	1259	34348	7739	466	1140	28598	4716	583	1024	26124	5163	7273	460	62100	1073
09/30/14	125	986	22127	6872																					7545	441	61522	1041
10/01/14	132	1093	23124	7206																					6017	503	53487	907
10/02/14	115	883	18350	5719	140	650	21375	3170	68	177	5365	269	229	927	24564	5429	61	594	15760	2585	41	330	10568	2054	7264	481	57066	1020
10/03/14	134	1071	22713	7024																					7210	495	58419	1041
10/04/14	117	920	20784	6474																					6234	441	54422	983
10/05/14	119	947	21382	6474																					5913	416	53324	979
10/06/14	138	900	22533	6976	158	740	24254	3615	84	340	7156	385	301	1158	32008	7249	504	1210	29899	4922	580	996	24490	4729	6417	485	56839	1026
10/07/14	121	1069	21604	6761																					5350	449	52204	960
10/08/14	130	991	20636	6303																					5902	415	54660	964
10/09/14	129	1006	21382	6579	164	684	23061	3435	100	395	7919	405	305	1133	31404	6898	348	1076	26845	4345	649	1146	27067	5361	5865	492	55156	1012
10/10/14	127	880	19209	5965																					5305	379	49464	923
10/11/14	120	855	18808	5782																					4642	324	43829	795
10/12/14	153	854	19076	5769																					5046	456	52880	990
10/13/14	129	914	19498	5956	154	594	20524	2991	98	327	7977	402	230	918	25254	5484	384	1027	24998	4022	633	996	24868	4966	5436	438	54038	1003
10/14/14	141	864	21220	6544																					5413	508	54714	1043
10/15/14	129	853	20438	6323																					4968	508	53513	1025
10/16/14	136	856	20316	6170	162	626	23035	3454	93	288	7797	433	222	786	22638	5064	361	972	26357	4168	450	738	18229	3549	4714	471	53517	994
10/17/14	130	764	18625	5733																					5211	419	53754	989
10/18/14	127	760	16882	5150																					4256	382	47388	893

Remediated Nitrate Salt Container Headspace Gas Analysis

	68685				69553				69615				69616				SB50069				SB50452				SB50522			
Date	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm
10/19/14	104	534	13567	4122																					4335	380	45197	861
10/20/14	153	755	19774	5992	173	650	22240	3287	97	327	7571	427	273	945	26484	5831	489	1065	26270	4161	485	694	20069	3872	4462	441	49670	948
10/21/14	128	798	17903	5509																					4713	441	55196	1045
10/22/14	122	720	19404	5908																					4001	448	54311	975
10/23/14	109	686	15847	4840	151	636	21460	3158	90	310	7198	441	172	621	18176	3941	326	825	19838	3094	467	733	19174	3714	3714	382	43891	871
10/24/14	128	726	16887	5117																					4069	462	47369	913
10/25/14	127	794	17673	5362																					4306	485	50341	973
10/26/14	129	815	17205	5166																					4303	482	50350	988
10/27/14	132	663	17151	5155	70	258	9559	1412	91	307	6680	367	296	951	25076	5452	321	855	21509	3300	682	1011	24026	4622	4059	416	45838	863
10/28/14	92	532	13283	4001	165	538	19975	2899																	4331	459	49603	990
10/29/14	122	593	14609	4395																					3824	409	45178	877
10/30/14	125	675	15264	4522	167	624	21345	3115	99	326	7475	427	269	905	24867	5381	486	1040	24911	3867	592	771	20419	3929	3636	404	46661	929
10/31/14	125	601	15788	4701																					4047	445	48930	933
11/01/14	125	643	15466	4618																					4084	472	48638	927
11/02/14	117	543	13498	3922																					3412	339	44406	868
11/03/14	125	659	16302	4871	166	581	19538	2813	103	309	7068	405	299	957	26831	5757	508	975	25480	4132	600	914	21858	4185	3677	525	48037	940
11/04/14	114	656	16116	4776																					3607	435	46770	899
11/05/14	129	637	16075	4832																					3250	461	43336	831
11/06/14	134	659	17053	5027	183	635	21958	3195	105	349	7821	460	325	966	28725	6286	495	1074	25294	3862	662	932	22070	4255	4165	546	52666	1037
11/07/14	134	674	17064	5074																					3212	414	45138	889
11/08/14	132	658	14129	4209																					3627	433	43345	865
11/09/14	129	628	15133	4483																					3418	390	47151	921
11/10/14	113	609	14383	4196	174	664	20355	2916	89	261	7255	402	310	1047	26352	5727	500	1090	24842	3721	515	789	19451	3751	3035	387	42716	847
11/11/14	115	510	13292	3888																					2594	367	40652	802
11/12/14	144	641	16464	4759																					3726	477	51417	1030
11/13/14	134	639	15710	4648	173	578	19488	2880	86	271	5996	297	313	1005	26779	5764	193	587	16004	2346	548	786	19664	3819	2646	414	43153	866
11/14/14	138	662	15957	4705													496	1006	24452	3607					3472	423	46087	966
11/15/14	100	464	10957	3148																					3351	444	46422	971
11/16/14	133	634	13689	3939																					3033	343	41196	863
11/17/14	136	582	14704	4200	172	619	19398	2861	94	302	7078	429	339	1060	27270	5895	505	1003	24070	3538	536	784	18936	3638	3193	386	44938	947
11/18/14	141	535	15443	4502																					3227	424	47350	984
11/19/14	131	599	15363	4419																					2942	394	47299	981
11/20/14	122	520	12991	3720	179	640	19188	2747	96	289	6912	369	317	1049	27007	5756	392	809	20400	2949	615	872	20575	4005	2904	465	44413	893
11/21/14	138	633	14509	4123																					2883	422	42319	876
11/22/14	141	540	15112	4274																					2957	409	44308	937
11/23/14	131	610	14298	4189																					2359	410	40768	948
11/24/14	138	562	15133	4365	185	602	18614	2806	108	294	7038	373	345	1020	27069	5789	498	939	23719	3425	690	923	21923	4186	2251	369	35824	775
11/25/14	116	448	12843	3665																					2782	474	46483	980
11/26/14	104	488	12307	3516	169	555	16017	2308	95	305	6311	343	319	847	22865	4874	378	671	18195	2674	535	773	18187	3488	2019	336	34189	741
11/27/14	126	608	14022	4054																					2608	460	43059	1020
11/28/14	127	598	13335	3807																					2353	403	39888	890
11/29/14	125	563	12897	3637																					2157	411	38811	835
11/30/14	129	476	11598	3330																					2087	361	36126	766
12/01/14	118	404	10983	3111	185	564	17517	2488	103	245	6440	342	305	718	20903	4529	492	870	20893	2918	603	696	15668	2990	2440	433	40385	902
12/02/14	132	502	13366	3809																					2231	405	40280	920
12/03/14	128	537	13467	3833																					2247	404	38377	911
12/04/14	96	401	10068	2802	188	627	17737	2511	88	228	5746	295	256	788	20840	4434	435	897	20480	2887	574	745	17186	3240	2259	398	39674	854
12/05/14	123	541	12591	3495																					2095	394	39617	965
12/06/14	133	593	11909	3337																					2294	431	38224	842
12/07/14	124	556	11892	3398																					2304	416	40170	875
12/08/14	135	496	11250	3145	164	503	16782	2390	106	276	6283	304	334	843	21506	4440	501	869	19749	2644	644	790	18735	3131	2237	440	38393	882

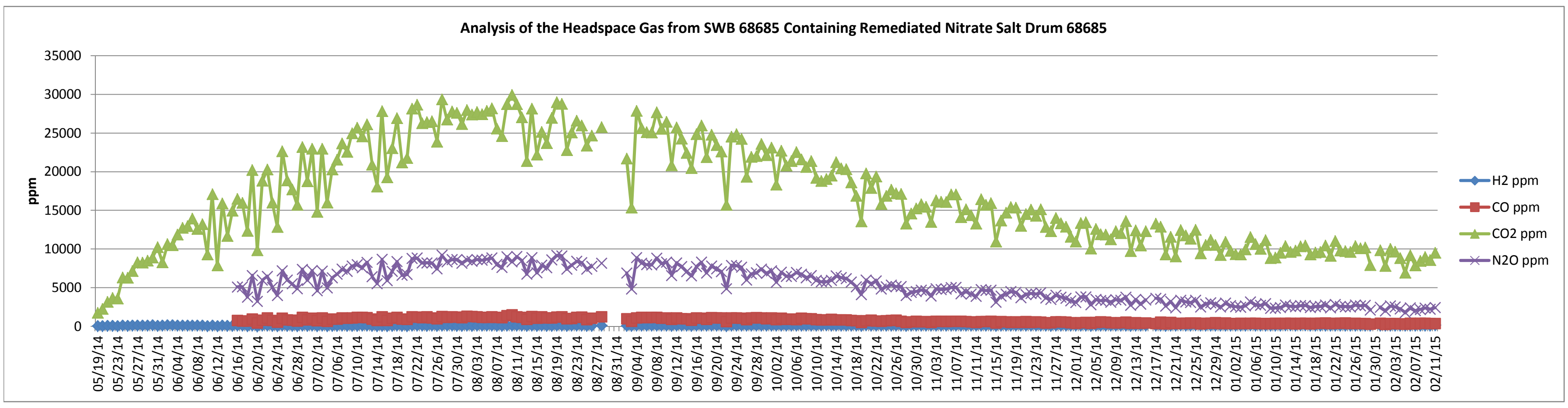
Remediated Nitrate Salt Container Headspace Gas Analysis

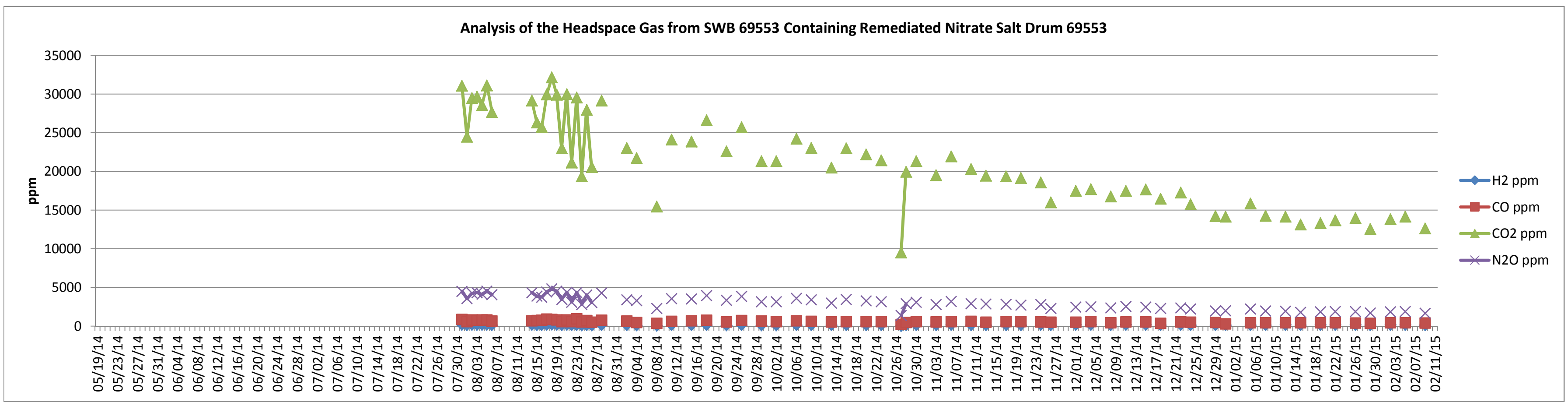
	68685				69553				69615				69616				SB50069				SB50452				SB50522			
Date	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm	H_2 ppm	CO ppm	CO_2 ppm	N_2O ppm
12/09/14	120	452	12299	3466																					1775	337	35927	801
12/10/14	138	475	12070	3387																					2390	483	40903	907
12/11/14	143	547	13614	3776	185	592	17536	2539	110	300	7047	329	354	897	24501	5101	499	967	21855	2953	701	836	19541	3605	2468	417	44340	983
12/12/14	99	400	9727	2743																					1695	291	30247	689
12/13/14	122	505	12431	3489																					2305	420	41194	903
12/14/14	125	423	10475	2867																					1856	411	36785	838
12/15/14	140	448	12315	3432	189	602	17715	2494	109	303	6748	323	323	854	23050	4765	412	835	20035	2708	615	807	17733	3313	2168	404	39337	892
12/16/14																												
12/17/14	144	381	13292	3658																					2517	506	44687	944
12/18/14	127	567	12880	3545	160	424	16517	2283	99	266	6911	355	274	627	19605	4044	504	937	21338	2848	536	704	16795	3080	2014	445	40037	906
12/19/14	103	361	9291	2643																					2126	503	41276	963
12/20/14	142	527	11601	3231																					1891	428	37671	902
12/21/14	126	376	9055	2428																					2270	431	37711	877
12/22/14	153	412	12475	3399	197	595	17299	2377	110	308	6905	358	350	926	23176	4782	504	999	20982	2767	658	779	18408	3421	1943	469	38733	902
12/23/14	134	402	11759	3179																					2307	462	42274	1014
12/24/14	135	468	11338	3090	179	571	15780	2211	87	288	6041	292	355	906	23103	4759	503	878	20733	2815	616	701	17591	3247	1823	392	39359	924
12/25/14	150	460	12482	3391																					2180	456	39958	944
12/26/14	126	329	9459	2507																					2050	449	35925	899
12/27/14	137	415	10530	2887																					1959	405	35946	868
12/28/14	138	427	11207	3079																					1591	310	34141	836
12/29/14	137	478	10528	2898	174	517	14269	1965	94	261	5813	291	277	742	19640	4056	497	961	19867	2643	441	554	12108	2273	1696	410	34618	857
12/30/14	124	364	9214	2514																					1857	431	34530	798
12/31/14	131	447	10945	3012	146	354	14194	2005	97	258	6778	368	303	861	20969	4254	180	649	15602	2136	667	675	16231	2965	1870	410	36196	920
01/01/15	136	364	9774	2691													444	806	17013	2283					1916	435	35242	872
01/02/15	130	393	9349	2568																					1780	378	33109	791
01/03/15	134	400	9306	2502																					1802	385	33184	844
01/04/15	129	378	9949	2667																					1717	375	34290	870
01/05/15	150	421	11541	3181	173	480	15874	2229	108	279	6961	345	364	868	22438	4615	313	752	18508	2456	619	723	15940	3010	1912	463	39690	971
01/06/15	142	434	10642	2798																					1700	459	38470	966
01/07/15	134	367	10024	2728																					1837	497	40582	1056
01/08/15	143	382	11155	2968	147	501	14281	1965	96	271	6776	371	299	807	21347	4470	223	708	16417	2176	644	690	15209	2842	1742	463	39865	1114
01/09/15	123	390	8839	2346																					1512	405	33851	799
01/10/15	125	417	8918	2380																					1636	479	35342	874
01/11/15	130	390	9510	2459																					1319	369	30532	788
01/12/15	150	415	10402	2760	191	504	14187	1948	109	318	6448	294	344	815	20433	4125	510	926	19496	2497	707	781	15560	2894	1765	419	38381	970
01/13/15	149	399	9647	2608																					1654	407	34812	841
01/14/15	137	357	9822	2556																					1509	409	35704	894
01/15/15	149	426	10341	2690	152	485	13172	1795	103	315	6118	282	351	799	20142	3997	509	857	19339	2480	667	746	15491	2874	1667	474	37855	1002
01/16/15	148	412	10468	2703																					1436	408	35349	899
01/17/15	120	333	9298	2454																					1569	448	33924	845
01/18/15	136	408	9539	2560																					1667	397	34182	887
01/19/15	142	402	9618	2586	183	474	13363	1849	107	249	6092	264	347	801	20009	4089	454	838	19086	2413	736	711	15349	2842	1670	419	36214	922
01/20/15	140	459	10454	2788																					1513	439	35942	912
01/21/15	133	398	9113	2399																					1700	462	36345	970
01/22/15	144	400	11050	2860	184	492	13700	1898	105	298	6560	328	315	694	18549	3768	397	786	18061	2317	669	640	14583	2690	1760	434	39451	1039
01/23/15	115	412	9820	2585																					1451	419	33614	863
01/24/15	135	436	9725	2574																					1593	470	35044	927
01/25/15	141	395	9639	2531																					1683	463	33929	870
01/26/15	144	415	10390	2758	193	459	14017	1900	112	294	6563	289	360	812	20869	4246	484	886	19729	2519	730	746	15937	2961	1779	473	37814	1002
01/27/15	142	385	10095	2678																					1551	414	36111	943
01/28/15	135	387	10214	2744																					1506	427	36016	951

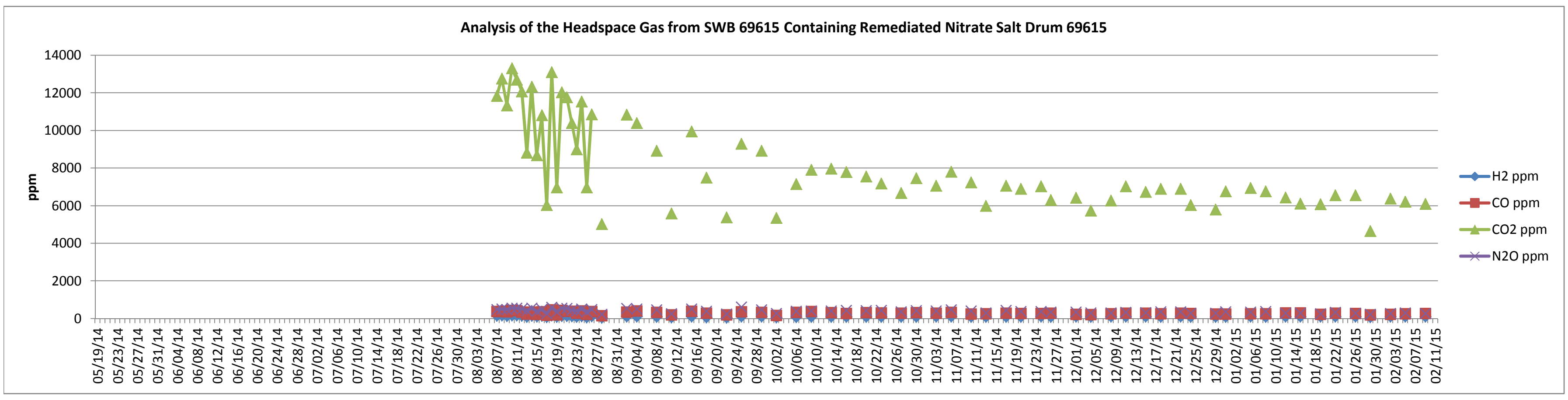
Remediated Nitrate Salt Container Headspace Gas Analysis

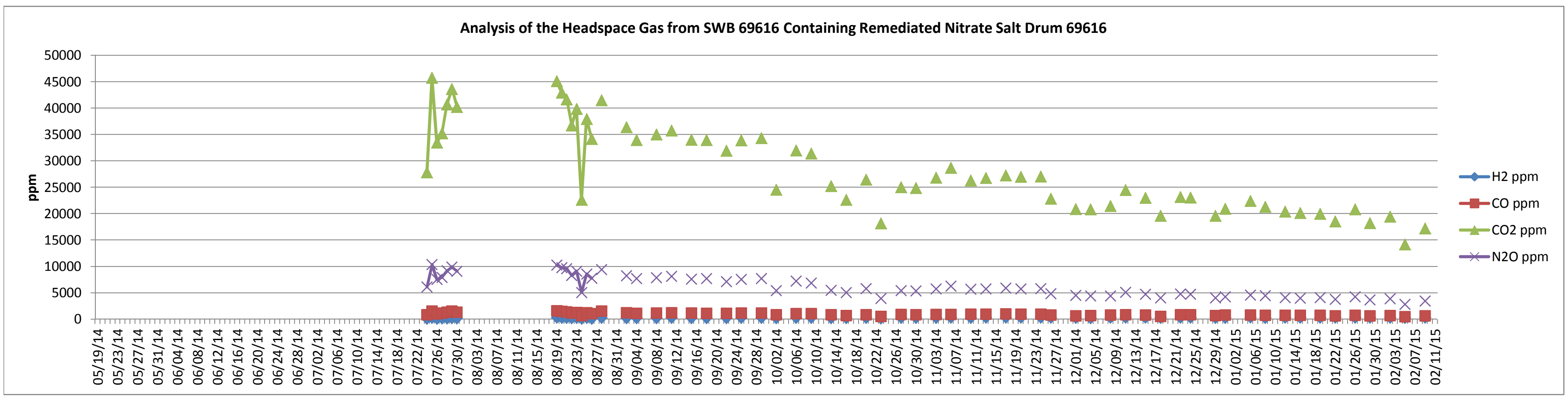
	68685				69553				69615				69616				SB50069				SB50452				SB50522			
Date	**H_2 ppm**	**CO ppm**	**CO_2 ppm**	**N_2O ppm**	**H_2 ppm**	**CO ppm**	**CO_2 ppm**	**N_2O ppm**	**H_2 ppm**	**CO ppm**	**CO_2 ppm**	**N_2O ppm**	**H_2 ppm**	**CO ppm**	**CO_2 ppm**	**N_2O ppm**	**H_2 ppm**	**CO ppm**	**CO_2 ppm**	**N_2O ppm**	**H_2 ppm**	**CO ppm**	**CO_2 ppm**	**N_2O ppm**	**H_2 ppm**	**CO ppm**	**CO_2 ppm**	**N_2O ppm**
01/29/15	137	325	7937	2124	179	426	12607	1704	76	211	4668	230	340	733	18253	3685	447	739	15462	1981	626	448	10331	1922	1605	375	30647	760
01/30/15																												
01/31/15	135	403	9843	2480																					1632	430	36921	1026
02/01/15	127	268	7811	2019																					1450	393	31354	958
02/02/15	141	375	10046	2657	195	482	13877	1868	109	249	6383	278	350	765	19472	3905	465	870	19027	2439	711	648	14712	2710	1759	423	36243	989
02/03/15	139	394	9655	2538																					1805	522	36846	985
02/04/15	143	355	8814	2263																					1559	424	33844	887
02/05/15	125	312	6948	1802	191	475	14172	1895	110	276	6229	296	309	552	14185	2811	446	707	15898	2004	633	519	11405	2080	1865	483	35436	1076
02/06/15	138	423	9203	2403																					1684	441	33286	929
02/07/15	126	349	7893	2038																					1727	416	30936	835
02/08/15	129	415	8455	2197																					1403	343	29184	780
02/09/15	136	421	8964	2393	150	454	12646	1685	105	293	6099	276	337	712	17234	3463	485	851	18429	2320	687	653	14005	2543	1868	432	33711	887
02/10/15	141	364	8560	2236																					2021	496	36359	968
02/11/15	146	380	9538	2446																					2052	529	36951	996

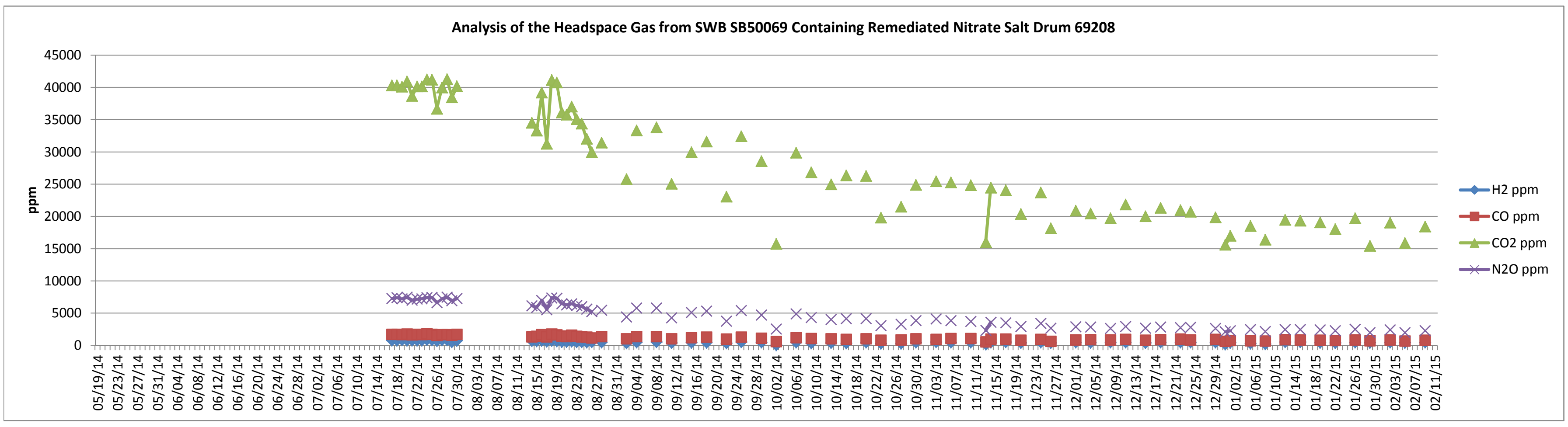
Remediated Nitrate Salt Container Headspace Gas Analysis

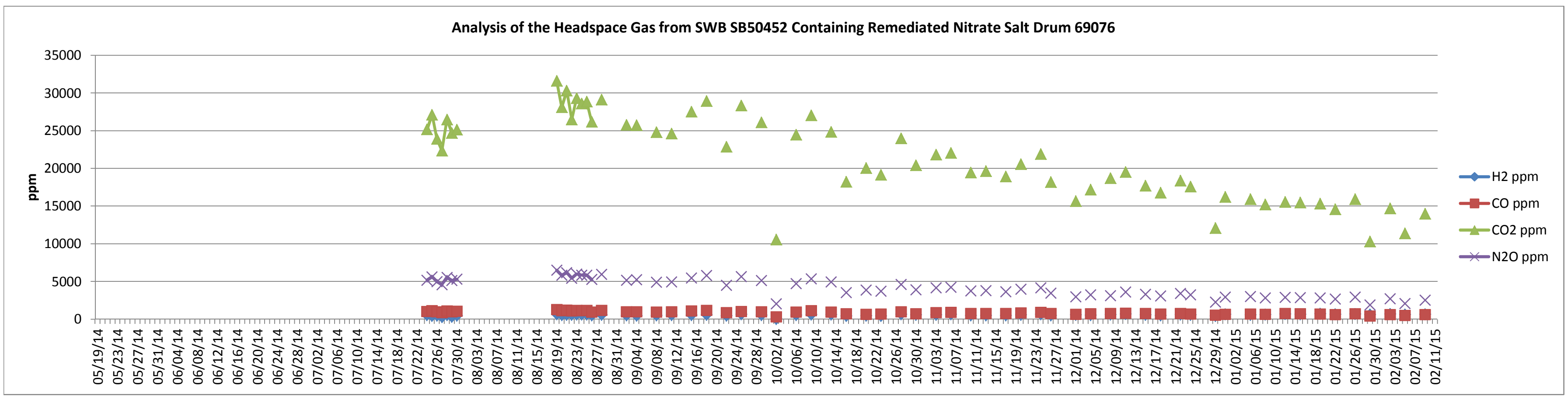




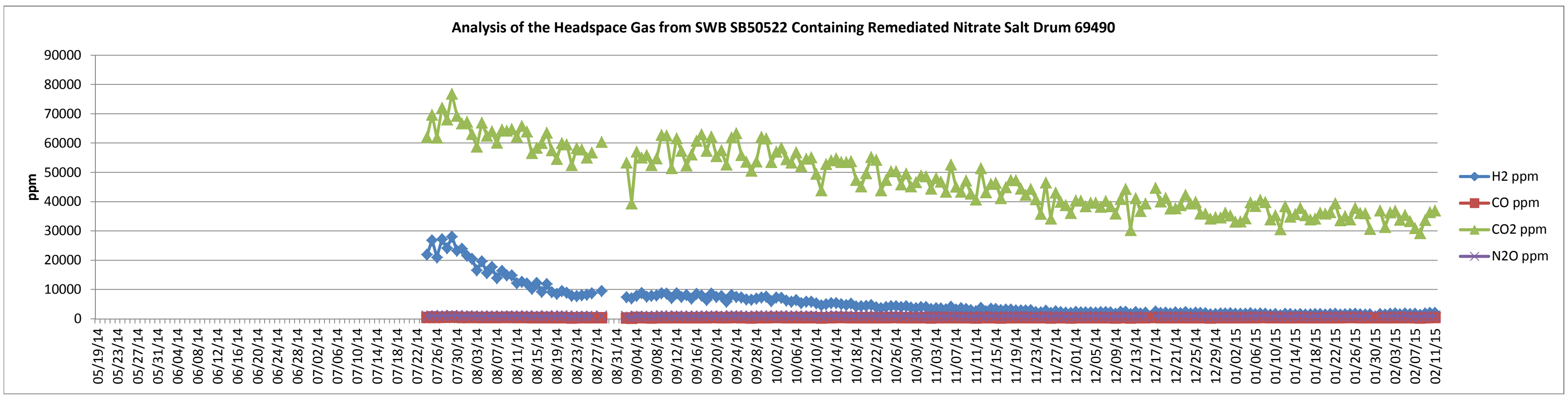








Remediated Nitrate Salt Container Headspace Gas Analysis



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Appendix 2

Table 1. Test Matrix for Swheat Kitty Litter Reactivity I. Reactivity Studies of SWheat Kitty litter mixtures.

Test Series 0	Nitrate Source	Acid Conc.	Neutralizing Agent	Product Sensitivity and Thermal Testing WX-7 Analytical Report #51924
Swheat Kitty Litter mixed wet	KNO_3	None	None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter ground and mixed dry	KNO_3		None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter wet and allowed to dry	KNO_3 dissolved in water		None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter nitrated under forcing conditions	None	Concentrated nitric and sulfuric	None	Impact, ESD, friction, DSC, vacuum stability- moderately sensitive, decomposes above 100 C, fails vacuum stability
Swheat Kitty Litter ground and mixed dry	$NaNO_3$	None	None	Impact, ESD, friction, DSC **Results in WX-7 Analytical Report #51927**
Swheat Kitty Litter ground and mixed dry	$NaNO_3$/ KNO_3 (1:1)	None	None	Impact, ESD, friction, DSC **Results in WX-7 Analytical Report #51927**

Test Series I	**Nitrate Source**	**Acid Conc.**	**Neutralizing Agent**	**Product Sensitivity and Thermal Testing WX-7 Analytical Report #51934, #51947**
Swheat Kitty Litter*	$NaNO_3$	16M HNO_3	None	Impact, ESD, friction, DSC, Analytical Report #51932
Swheat Kitty Litter*	$NaNO_3$	0.001M HNO_3	None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter*	$NaNO_3$	1M HNO_3	None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter*	$NaNO_3$	5M HNO_3	None	Impact, ESD, friction, DSC, vacuum stability - fails vacuum stability
Swheat Kitty Litter*	$NaNO_3$	8M HNO_3	None	Impact, ESD, friction, DSC, vacuum stability - fails vacuum stability. Onset at 121 ˚C. Analytical Lab Report #51956.
Swheat Kitty Litter*	$NaNO_3$	16M HNO_3	None	Impact, ESD, friction, DSC, vacuum stability - fails vacuum stability Onset at 101 ˚C. Analytical Lab Report #51956.
Swheat Kitty Litter* Aging Studies	$NaNO_3$	0.001, 1M and 5M HNO_3	None	data has not varied over time to date (Analytical Report 51981 has VTS and DSC at 2 months. 5M HNO_3 mix fails VTS.) 2 week data is in #51947.

Test Series II	**Nitrate Source**	**Acid Conc.**	**Neutralizing Agent**	**Reactivity, thermal stability studies, and degradation product isolation and identification**
Swheat Kitty Litter*	$NaNO_3$	0.001M HNO_3	None	Head space analysis at ambient temperature & 80C; nuclear magnetic resonance spectroscopy to characterize products
Swheat Kitty Litter*	$NaNO_3$	1M HNO_3	None	Head space analysis at ambient temperature and 80C; nuclear magnetic resonance spectroscopy to characterize products
Swheat Kitty Litter*	$NaNO_3$	5M HNO_3	None	Head space analysis at ambient temperature and 80C; nuclear magnetic resonance spectroscopy to characterize products

Test Series III (partially completed)	**Nitrate Source**	**Acid Conc.**	**Neutralizing Agent**	**Product Sensitivity (WX-7 Analytical Report #51933), Thermal Testing, and degradation product isolation and identification**
Swheat *	$NaNO_3$	1M and 5M HNO_3	Kolorsafe Neutralizer Triethanol-amine (TEA)	Impact, ESD, friction, DSC, vacuum stability; Head space analysis at ambient temperature and 80C; nuclear magnetic resonance spectroscopy to characterize products
Triethanolamine nitrate salt (TEAN)	None	None	None	Impact, ESD, friction, DSC, vacuum stability; Head space analysis at ambient temperature and 80C; nuclear magnetic resonance spectroscopy to characterize products

*1:3 ratio $NaNO_3$ to SWheat by volume, superstaturated solutions of $NaNO_3$ with the indicated HNO_3 conc.

**1M HNO3 saturated with NaNO3 titrated neutralized with TEA, addition of 0.3 wt% $NaNO_2$ then 3 volumes of SWheat kitty litter

Table 2. Test Matrix for Swheat Kitty Litter Reactivity II. Reactivity Studies of SWheat Kitty litter mixtures with Lead and Tungsten.

Test Series I	**Nitrate Source**	**Acid Concentration**	**Neutralizing Agent**	**Product Sensitivity and Thermal Testing, characterization**
Triethanolamine	HNO_3	1M HNO_3	None	Look for formation of nitrate esters
Triethanolamine	HNO_3	7M HNO_3	None	Look for formation of nitrate esters
Triethanolamine	HNO_3	16M HNO_3	None	Look for formation of nitrate esters- unstable with NO_2 production within 1-2 days
Test Series II	**Metal source**	**Acid Concentration**	**Neutralizing Agent**	**Reactivity and, thermal stability studies, and breakdown product isolation and identification**
Swheat Kitty Litter*	Pb flake	1M HNO_3	None	DSC, vacuum stability. Analytical Report #51956
Swheat Kitty Litter*	Pb flake	7M HNO_3	None	DSC, vacuum stability – exotherm onset 121 C. Analytical Report #51956
Swheat Kitty Litter*	Pb flake	16M HNO_3	None	DSC, vacuum stability - exotherm onset 101 C. Analytical Report #51956
Swheat Kitty Litter*	W **	1M HNO_3	none	DSC, vacuum stability. Analytical Report #51955
Swheat Kitty Litter*	W **	7M HNO_3	none	DSC, vacuum stability – exotherm onset 106 C. Analytical Report #51955
Swheat Kitty Litter*	W **	16M HNO_3	none	DSC, vacuum stability – exotherm onset 98 C. DSC and VTS in Analytical Report #51955
Test Series III	**Nitrate Source**	**Acid Concentration**	**Metal source**	**Product Sensitivity, Thermal Testing, and breakdown product isolation and identification**
Triethanolamine nitrate/Swheat	$NaNO_3$	1M, 7M, 16M	Pb	DSC, vacuum stability. Head space analysis at ambient temperature and 80C; nuclear magnetic resonance spectroscopy to characterize products - exotherm onset 108 C. Analytical Report #51958
Triethanolamine nitrate salt/Swheat	$NaNO_3$	1M, 7M, 16M	W**	DSC, vacuum stability. Head space analysis at ambient temperature and 80C; nuclear magnetic resonance spectroscopy to characterize products - exotherm onset 109 C. Analytical Report #51959

*1:3 ratio $NaNO_3$ to SWheat by volume, superstaturated solutions of $NaNO_3$ in the indicated HNO_3

W** - tungsten lined glove is the source

Table 3. Test Matrix for SWheat Kitty Litter Reactivity III. Reactivity studies of mixtures with Lead and Tungsten dissolved in acid prior to mixing.

Table 3. Test Matrix for SWheat Kitty Litter Reactivity III

Test Series I	**Metal Source**	**Acid Concentration**	**Other**	**Thermal Testing, characterization (Differential Scanning Calorimetry/DSC, Vacuum Thermal Stability, Thermal Activity Monitor/TAM, Adiabatic Pressure Tracking Accelerated Calorimetry/APTAC)**
Swheat Kitty Litter*	Pb’	1M HNO$_3$	None	DSC, Vacuum stability, Analytical Report #51956
Swheat Kitty Litter*	Pb’	8M HNO$_3$	None	DSC, Vacuum stability, Analytical Report #51956
Swheat Kitty Litter*	Pb’	16M HNO$_3$	None	DSC, Vacuum stability, Analytical Report #51956
Swheat Kitty Litter*	Pb’	1M, 8M, 16M HNO$_3$	W-lined glove	DSC, Vacuum stability, Analytical Report #51955
Swheat + nitric acid and TEAN	Pb’	None, 1 M, 8M HNO$_3$	none	DSC, Vacuum stability. Onset at 108 ˚C in 8M and failed VTS. Analytical Lab #51958
Swheat + nitric acid and TEAN	W**	None, 1 M, 8M HNO$_3$	none	DSC, Vacuum stability. Onset at 109 ˚C in 8M and failed VTS. Analytical Lab #51959
Swheat + nitric acid	W**	1 M, 8M, 16M HNO$_3$	none	DSC, Vacuum stability. 8M and 16 M failed VTS. Analytical Lab #51979
Swheat + nitric acid and TEAN	Pb’	None, 1 M, 16M HNO$_3$	none	DSC, Vacuum stability. 8M and 16 M failed VTS. Analytical Lab #51980
Test Series II	**Metal source**	**Acid Concentration**	**Neutralizing Agent**	**Thermal Activity Monitor (TAM), Adiabatic pressure tracking accelerated rate calorimetry(APTAC)**
Swheat Kitty Litter*	N/A	pH 7 (no acid; salt is wet)	none	TAM, APTAC (weak pressure rise, no measurable thermal activity)
Swheat Kitty Litter*	N/A	16M HNO$_3$	none	TAM APTAC (weak pressure rise, no measurable thermal activity)
Swheat Kitty Litter*	Pb flake	1M HNO$_3$	None	APTAC
Swheat Kitty Litter*	Pb flake	8M HNO$_3$	None	TAM (@55 C, exotherm after 5 hours, 5 W/g), Analytical Lab #51968
Swheat Kitty Litter*	Pb flake	16M HNO$_3$	None	TAM (@55 C, exotherm after 12 hours, 20 W/g), APTAC (weak pressure rise), Analytical Lab #51968
Swheat Kitty Litter*	W **	1M HNO$_3$	none	APTAC
Swheat Kitty Litter*	W **	8M HNO$_3$	none	TAM, APTAC
Swheat Kitty Litter*	W **	16M HNO$_3$	none	TAM, APTAC

Test Series III	**Nitrate Source**	**Acid Concentration**	**Metal source**	**Product Sensitivity, Thermal Testing, and breakdown product isolation and identification**
Triethanolamine nitrate/Swheat	$NaNO_3$	1M$^{\#}$, 8M, 16M	Pb	TAM, APTAC
Triethanolamine nitrate salt/Swheat	$NaNO_3$	1M$^{\#}$, 8M, 16M	W**	TAM, APTAC
*1:3 ratio $NaNO_3$ to SWheat by volume, superstaturated solutions of $NaNO_3$ in the indicated HNO_3 Pb' – lead dissolved in the associated acid W** - tungsten lined glove is the source				

Table 4. Mixed Nitrate Tests. Other analytical testing of relevant mixtures.

Test Series I (completed)	**Nitrate Source and inorganic materials**	**Acid Concentration**	**Product Sensitivity and Thermal Testing, characterization**
Swheat Kitty Litter	None	None	CHN elemental analysis. Analytical Report #51963.
Water washed samples	?	?	CHN elemental analysis. Analytical Report #51990
4% HNO3, 21%NaNO3,75% Swheat			DSC and TGA. Analytical Report #51941
6-14N, D (Chamberlin-Yarbro)			Sensitivity testing. Analytical Report #51983. MSR WX-7-AC-14-068U
SFWB3	Al(NO3)3 * 9 H20, Ca(NO3)2 * 4 H2O, KNO3, Cr(NO3)3 * 9H2O, Fe(NO3)3 * 9H2O, Mg(NO3)2 * 6H2O, NaNO3, Ni(NO3)2 * 6H2O, Pb(NO3)2, NaF	5 wt% 4M HNO_3 1.1 wt% oxalic	DSC, TAM, APTAC, sensitivity testing. Analytical Report #52004. CHN #52002
SFWB4	Ca(NO3)2 * 4 H2O, Cr(NO3)3 * 9H2O, Fe(NO3)3 * 9H2O, Mg(NO3)2 * 6H2O, NaNO3, Pb(NO3)2	1.4 wt% oxalic	DSC, TAM, APTAC, sensitivity testing. Analytical Report #52013, MSR
SFWBi2O3 aged	Ca(NO3)2 * 4 H2O, Cr(NO3)3 * 9H2O, Fe(NO3)3 * 9H2O, Mg(NO3)2 * 6H2O, NaNO3, Pb(NO3)2, Bi_2O_3	1.4 wt% oxalic	DSC, TAM, APTAC, sensitivity testing. MSR
SFWBi2O3 unaged	Ca(NO3)2 * 4 H2O, Cr(NO3)3 * 9H2O, Fe(NO3)3 * 9H2O, Mg(NO3)2 * 6H2O, NaNO3, Pb(NO3)2, Bi_2O_3	1.4 wt% oxalic	Sensitivity testing. MSR

Table 5. Chemical compositions of samples studied with calorimetry. Numerical entries are weight percentages.

Chemical	NEXT 1	NEXT2	NEXT3	NEXT4	WB-3	WB-4	WB-4-2
Al(NO3)3 * 9 H20	0.0	0.0	0.0	0.0	1.8	0.0	0.0
Ca(NO3)2 * 4 H2O	8.4	8.4	8.4	8.4	7.2	8.4	9.7
KNO3	0.0	0.0	0.0	0.0	1.6	0.0	0.0
Cr(NO3)3 * 9H2O	0.0	0.0	0.0	0.0	0.1	0.1	0.1
Fe(NO3)3 * 9H2O	7.7	10.0	10.0	10.0	4.8	5.7	6.7
H2O	0.2	0.2	0.2	0.2	0.0	0.2	0.2
Mg(NO3)2 * 6H2O	21.0	21.0	27.7	35.0	47.0	20.6	23.9
HNO3	0.0	0.0	0.0	0.0	0.8	0.0	0.0
NaNO3	36.6	34.3	27.6	20.3	10.3	36.7	42.5
NaF	0.0	0.0	0.0	0.0	0.2	0.0	0.0
Ni(NO3)2 * 6H2O	0.0	0.0	0.0	0.0	0.1	0.0	0.0
Pb(NO3)2	0.0	0.0	0.0	0.0	0.1	1.9	2.2
(COOH)2	1.1	1.1	1.1	1.1	1.1	1.4	1.6
Swheat	25.0	25.0	25.0	25.0	25.0	25.0	13.0

Table 5 (continued). Chemical compositions of samples studied with calorimetry. Numerical entries are weight percentages.

Chemical	WB-4-Fe	WB-4-Pb	WB-4-Cr	WB-5P	WB4Bi	WB-6P	PLA
Al(NO3)3 * 9 H20	0.0	0.0	0.0	1.8	0	0.0	0.0
Ca(NO3)2 * 4 H2O	9.2	8.4	8.4	7.2	8.4	0.0	7.5
KNO3	0.0	0.0	0.0	1.6		0.0	0.0
Cr(NO3)3 * 9H2O	0.2	0.1	0.0	0.1	0.1	0.0	0.0
Fe(NO3)3 * 9H2O	0.0	7.7	5.9	6.0	5.7	5.8	4.5
H2O	0.0	0.2	0.2	0.0	0.2	0.2	0.0
Mg(NO3)2 * 6H2O	22.5	20.6	20.6	44.0	20.6	29.0	41.3
HNO3	0.0	0.0	0.0	0.8	0.0	0.0	0.8
NaNO3	39.9	36.7	36.7	10.3	36.7	36.7	19.5
NaF	0.0	0.0	0.0	0.2	0.0	0.0	0.0
Ni(NO3)2 * 6H2O	0.0	0.0	0.0	0.1	0.0	2.0	0.0
Bi(NO3)2	0.0	0.0	0.0	0.0	1.9	0.0	0.0
Pb(NO3)2	2.1	0.0	1.9	1.9	0.0	0.0	0.0
(COOH)2	1.5	1.4	1.4	1.1	1.4	1.4	1.5
Swheat	24.6	25.0	25.0	25.0	25.0	25.0	25.0

Table 6. Sensitivity and Thermal Testing.

Material	Test Data	Analytical Lab #
WB-4-2	Impact, Friction, ESD, DSC, VTS	52013 (not yet complete, failed VTS)
WB4Bi	Impact, Friction, ESD, DSC, VTS	52045 (failed VTS)
WB4Bi, aged 60 ˚C for 12 hours	Impact, Friction, ESD, DSC, VTS	52045 (failed VTS)
WB-5P	Impact, Friction, ESD, DSC, VTS	52004 (failed VTS)

Table 7. Temperatures of Onsets of Self-Heating and Pressurization in the APTAC.

Material	APTAC Thermal Onsets (˚C)	APTAC Pressure Onsets (˚C)
WB-3	55, 255	55, 135, 255
WB-4	55, 100	55, 100, 260
WB-4-2	55, 100	55, 100, 150, 200
WB-4-Fe	None	95, 130, 200
WB4Bi	60	56
PLA	55	55, 100
SWheat + TEAN	163	163

Table 8. Times of Pressurization Onset in 60 ˚C TAM Experiments.

Material	TAM Pressure Onset Times (in hours after insertion)
NEXT 1	26.4
NEXT 2	19.7, 8.3 (2nd run)
NEXT 3	12.8, 12.5 (2nd run)
NEXT 4	9.7
WB4-Pb	23.6, 20.8 (2nd run)
WB4-Cr	34.7
WB-5P	13.9
WB-5P aged	20.8
WB-6P	61.0
WB4Bi	57.0
WB-3	25.8
WB-4	54.0
WB-4 aged	5.5 (weak), 38.9

Appendix 3

Analytical Chemistry and Materials Characterization Results for Debris Recovered from Four Nitrate Salt Waste Drums

October 24, 2014

Los Alamos
NATIONAL LABORATORY
EST. 1943

Executive Summary

Samples of solid debris, recovered from four previously remediated nitrate salt waste drums, were characterized using a variety of inorganic and radioanalytical methods. This work was performed to contribute to the understanding of possible chemistries in remediated nitrate salt wastes, and to develop and demonstrate the analytical flowsheets required for these sample types. Both objectives were met.

A concise profile of each drum's characteristics is presented, followed by details on the methods used. The debris is heterogeneous and consists mainly of lead nitrate and sodium nitrate particles, with smaller numbers of iron-rich particles. Other percent-level metal constituents are magnesium, aluminum, potassium, calcium, and uranium, and numerous other metals are present at levels <500 µg/g. Nitrate is the predominant anion at 15-21% of sample mass, with nitrite, chloride, fluoride and free oxalate anions contributing <0.5%. Volatile compounds (<200 ^{o}C) make up 15-37% of each drum sample's mass, while combustible materials (200-600 ^{o}C) contribute another 28-57%. Excluding the nitrates, the combustible fraction has a carbon content of 24-62%. Plutonium content varies from 50-500 µg/g, and americium-241 mass concentrations are typically 10-30% of the plutonium levels.

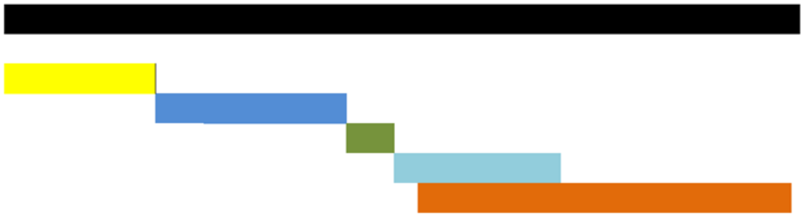
Drum S864694, overpack 69139

Contained 4 gallons of free liquid, pH 0.
Processed December, 2013
Daughters: 68681, 69061

Sampled 6/26/2014
17.98 g solid collected
Appearance: Heterogeneous, red-brown and off-white, free-flowing solid.

Composition Profile[1]

69139	**Weight %**
Volatiles (200 C)	**18.7**
Lead (Pb)	**24.2**
Other Metals	**5.7**
Nitrate	**21.4**
Combustibles (600 C)	**46.1**
Other Anions	**0.2**



Metals[2]

Lead (Pb, total)	24.2	wt%
Sodium (Na)	3.72	
Magnesium (Mg)	0.21	
Aluminum (Al)	0.60	
Calcium (Ca)	0.25	
Antimony (Sb)	44	μg/g
Beryllium (Be)	<0.2	
Bismuth (Bi)	42	
Boron (B)	154	
Cadmium (Cd)	14	
Copper (Cu)	340	
Gallium (Ga)	490	
Iron (Fe)	5400	
Manganese (Mn)	51	
Molybdenum (Mo)	34	
Nickel (Ni)	730	
Potassium (K)	360	
Silicon (Si)	78	
Thallium (Tl)	69	
Uranium (U)	620	
Yttrium (Y)	66	
Zinc (Zn)	110	

Non-Metals[3]

pH of absorbed liquid	1.8	
Available H^+ in solid	1.07	mol/kg
Volatiles (200 ^oC)	18.7	wt%
Combustibles (600 ^oC)	46.1	wt%
Nitrate (NO_3^-)	21.4	
Non-nitrate combustibles	27.8	
Carbon (C)	8.8	
(32 wt% of non-nitrate combustibles)		
Other anions		
Nitrite (NO_2^-)	600	μg/g
Fluoride (F^-)	70	
Chloride (Cl^-)	850	
Oxalate (free, $C_2O_4^{2-}$)	1400	

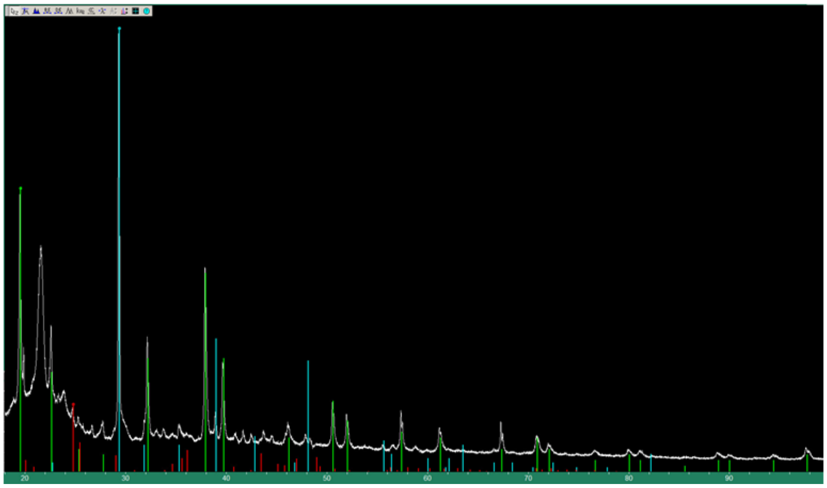
Drum S864694, overpack 69139

Direct Solids Characterization[4]

Powder X-ray Diffraction
(0-100 degrees plotted)

Confirmed:
Lead nitrate, $Pb(NO_3)_2$
Sodium nitrate, $NaNO_3$

Not observed, or low confidence: Lead carbonate, $PbCO_3$; Mg, Ca nitrates or oxalates; Iron oxide; Lead oxide; Lead oxalate

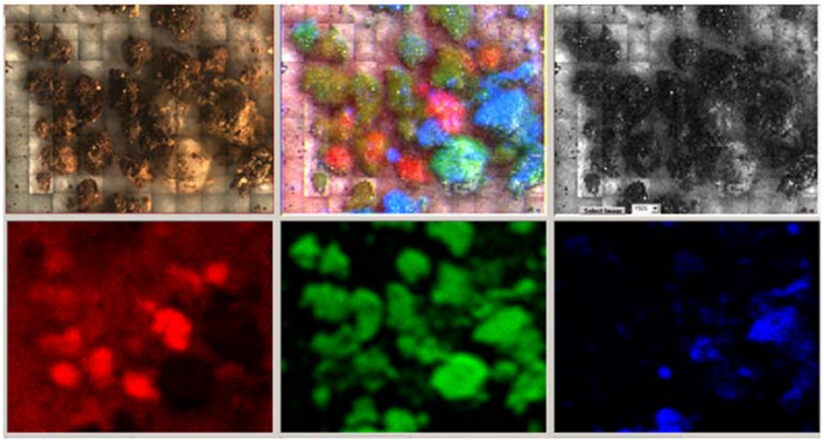


Micro X-ray Fluorescence
(25.1 mm x 19.6 mm area imaged)

Top row (L-R):
1. Visible light image
2. Composite of images 3-5
3. Greyscale

Bottom row (L-R):
4. Low-*Z* (Compton scatter)
5. Lead (Pb)
6. Iron (Fe)

Also detected: Cr, Ni, Cu, U, Pu



Radionuclides[5]

Non-Destructive Screening

Isotope	**µg / g**	**RSD**
^{238}Pu	--	
^{239}Pu	9.51e+02	(3.5%)
^{240}Pu	5.32e+01	(21%)
^{241}Pu	6.84e-01	(12%)
^{241}Am	1.22e+02	(3.4%)
^{243}Am	2.59e-01	(3.7%)
^{237}Np	5.41e+00	(3.6%)
^{235}U	5.89e+01	(11%)
^{238}U	--	

Destructive Analysis: Plutonium

Isotope	**atom%**
^{238}Pu	0.0014
^{239}Pu	93.7336
^{240}Pu	6.1915
^{241}Pu	0.0082
^{242}Pu	0.0653

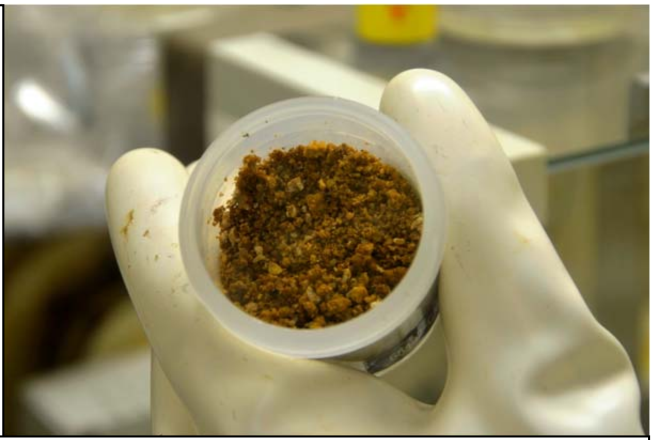
Total Pu 496 µg / g

Decay Heat 8 mW/kg solid (0.7%)

Drum S822952, overpack 68492

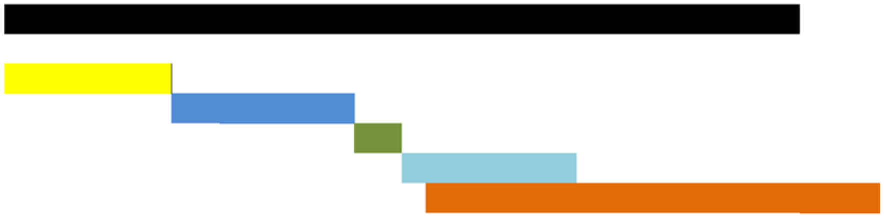
Contained 8 gallons of free liquid, pH not recorded.
Processed November, 2013
Daughters: 68573, 68605, 68607

Sampled 7/3/2014
27.85 g solid collected
Appearance: Heterogeneous, red-brown, free-flowing solid.



Composition Profile[1]

68492	Weight %
Volatiles (200 C)	20.6
Lead (Pb)	21.7
Other Metals	5.9
Nitrate	21.8
Combustibles (600 C)	57.3
Other Anions	0.5



Metals[2]

Lead (Pb, total)	21.7	wt%
Sodium (Na)	2.73	
Magnesium (Mg)	0.18	
Aluminum (Al)	0.33	
Calcium (Ca)	0.26	
Antimony (Sb)	1	µg/g
Beryllium (Be)	340	
Bismuth (Bi)	31	
Boron (B)	87	
Cadmium (Cd)	<2	
Copper (Cu)	200	
Gallium (Ga)	160	
Iron (Fe)	2800	
Manganese (Mn)	29	
Molybdenum (Mo)	6	
Nickel (Ni)	53	
Potassium (K)	2700	
Silicon (Si)	15	
Thallium (Tl)	43	
Uranium (U)	17300	
Yttrium (Y)	1	
Zinc (Zn)	190	

Non-Metals[3]

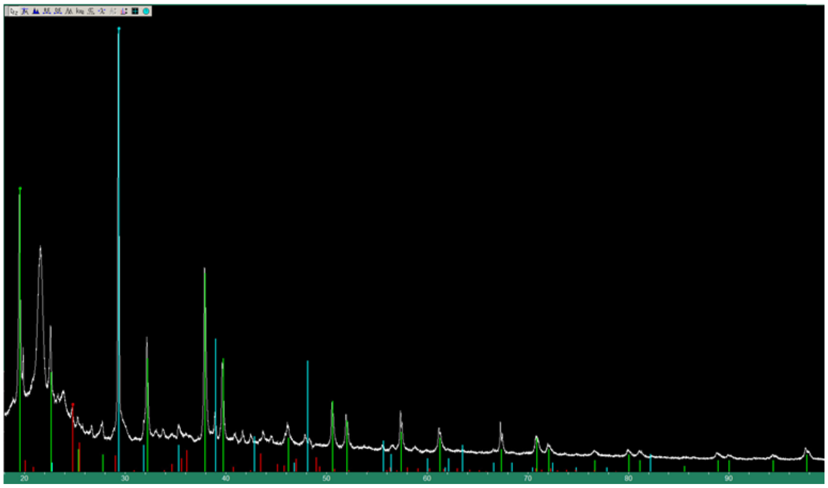
pH of absorbed liquid	1.6	
Available H^+ in solid	0.83	mol/kg
Volatiles (200 ^{o}C)	20.6	wt%
Combustibles (600 ^{o}C)	57.3	wt%
Nitrate (NO_3^-)	21.8	
Non-nitrate combustibles	38.6	
Carbon (C)	9.2	
(24 wt% of non-nitrate combustibles)		
Other anions		
Nitrite (NO_2^-)	50	µg/g
Fluoride (F^-)	1200	
Chloride (Cl^-)	380	
Oxalate (free, $C_2O_4^{2-}$)	2800	

Drum S822952, overpack 68492

Direct Solids Characterization

Powder X-ray Diffraction

(0-100 degrees plotted)



Confirmed:

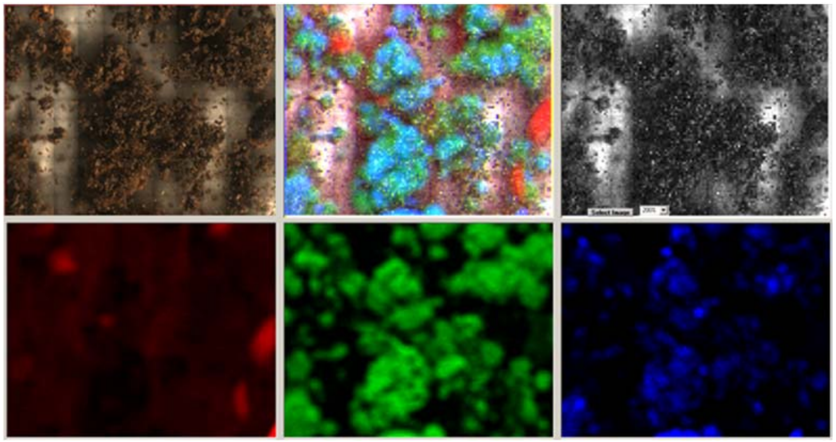
Lead nitrate, $Pb(NO_3)_2$

Sodium nitrate, $NaNO_3$

Not observed, or low confidence: Lead carbonate, $PbCO_3$; Mg, Ca nitrates or oxalates; Iron oxide; Lead oxide; Lead oxalate

Micro X-ray Fluorescence

(25.1 mm x 19.6 mm area imaged)



Top row (L-R):

1. Visible light image
2. Composite of images 3-5
3. Greyscale

Bottom row (L-R):

4. Low-*Z* (Compton scatter)
5. Lead (Pb)
6. Iron (Fe)

Also detected: K, Ca, Cr, Ni, Cu, Zn, U, and Pu

Radionuclides[5]

Non-Destructive Screening

Isotope	**µg / g**	**RSD**
^{238}Pu	3.03e-01	(11%)
^{239}Pu	9.26e+01	(4.5%)
^{240}Pu	8.94e+00	(28%)
^{241}Pu	3.91e-01	(11%)
^{241}Am	1.61e+01	(3.9%)
^{243}Am	1.94e-04	(23%)
^{237}Np	8.83e-01	(4.2%)
^{235}U	6.28e+01	(6.8%)
^{238}U	2.42e+04	(4.8%)

Destructive Analysis: Plutonium

Isotope	**atom%**
^{238}Pu	0.2387
^{239}Pu	69.0115
^{240}Pu	7.4556
^{241}Pu	0.3001
^{242}Pu	22.9941

Total Pu 83 µg / g

Decay Heat 2 mW/kg solid (4%)

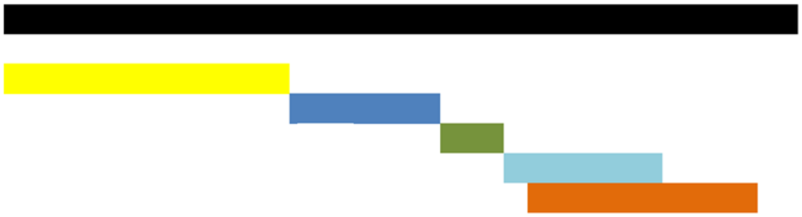
Drum S818449, overpack 68645

Contained 6 gallons of free liquid, pH 3.
Processed November, 2013
Daughters: 68630

Sampled 7/8/2014
18.20 g solid collected
Appearance: Heterogeneous, red-brown, very moist, clumping solid.

Composition Profile[1]

68645	**Weight %**
Volatiles (200 C)	**37.3**
Lead (Pb)	**18.9**
Other Metals	**8.0**
Nitrate	**19.1**
Combustibles (600 C)	**27.9**
Other Anions	**0.1**



Metals[2]

Lead (Pb, total)	18.9	wt%
Sodium (Na)	1.61	
Magnesium (Mg)	3.28	
Aluminum (Al)	2.12	
Calcium (Ca)	0.27	
Antimony (Sb)	16	µg/g
Beryllium (Be)	270	
Bismuth (Bi)	25	
Boron (B)	28	
Cadmium (Cd)	< 1	
Copper (Cu)	200	
Gallium (Ga)	470	
Iron (Fe)	2700	
Manganese (Mn)	22	
Molybdenum (Mo)	12	
Nickel (Ni)	120	
Potassium (K)	840	
Silicon (Si)	<10	
Thallium (Tl)	68	
Uranium (U)	1900	
Yttrium (Y)	85	
Zinc (Zn)	61	

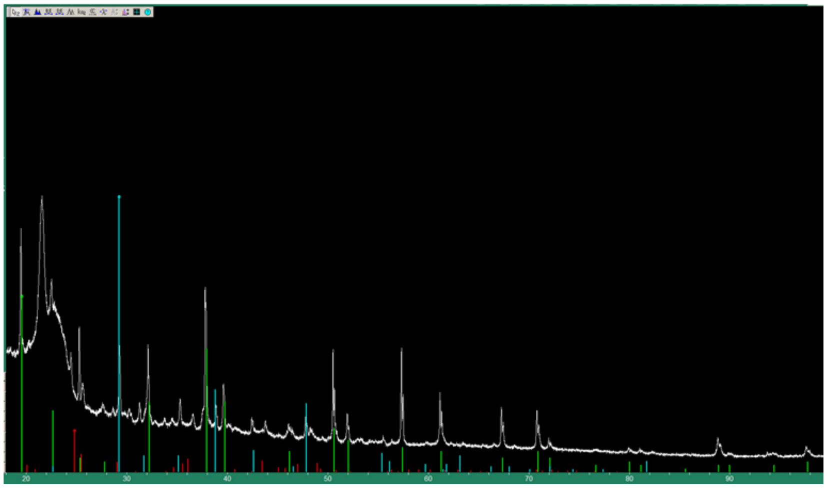
Non-Metals[3]

pH of absorbed liquid	2.5	
Available H^+ in solid	0.46	mol/kg
Volatiles (200 °C)	37.3	wt%
Combustibles (600 °C)	27.9	wt%
Nitrate (NO_3^-)	19.1	
Non-nitrate combustibles	11.6	
Carbon (C)	7.2	
(62 wt% of non-nitrate combustibles)		
Other anions		
Nitrite (NO_2^-)	640	µg/g
Fluoride (F^-)	12	
Chloride (Cl^-)	410	
Oxalate (free, $C_2O_4^{2-}$)	170	

Drum S818449, overpack 68645

Direct Solids Characterization

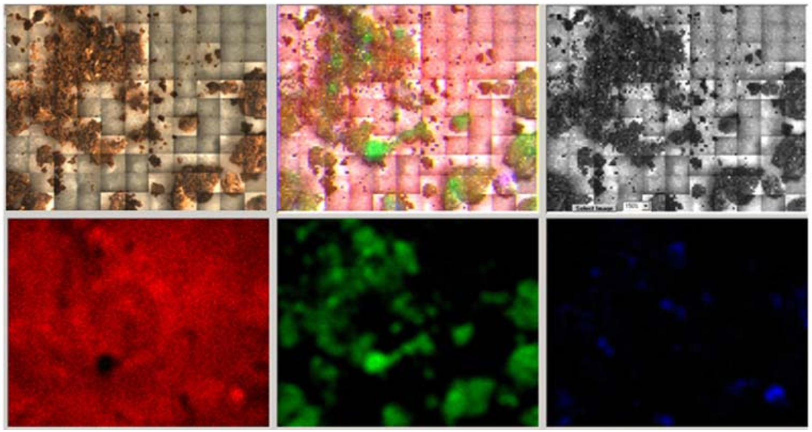
Powder X-ray Diffraction
(0-100 degrees plotted)



Confirmed:
Lead nitrate, $Pb(NO_3)_2$
Sodium nitrate, $NaNO_3$

Not observed, or low confidence: Lead carbonate, $PbCO_3$; Mg, Ca nitrates or oxalates; Iron oxide; Lead oxide; Lead oxalate

Micro X-ray Fluorescence
(25.1 mm x 19.6 mm area imaged)



Top row (L-R):

7. Visible light image
8. Composite of images 3-5
9. Greyscale

Bottom row (L-R):

10. Compton scatter (low-Z)
11. Lead (Pb)
12. Iron (Fe)

Also detected: K, Ca, Cr, Ni, Cu, Zn, Ga, U, and Pu.

Radionuclides[5]

Non-Destructive Screening

Isotope	µg / g	RSD
^{238}Pu	--	
^{239}Pu	2.44e+02	(4.9%)
^{240}Pu	--	
^{241}Pu	1.80e-01	(32%)
^{241}Am	7.86e+01	(3.8%)
^{243}Am	6.76e-04	(25%)
^{237}Np	2.95e+00	(3.9%)
^{235}U	6.21e+01	(12%)
^{238}U	4.20e+03	(26%)

Decay Heat 4 mW/kg solid (3%)

Destructive Analysis: Plutonium

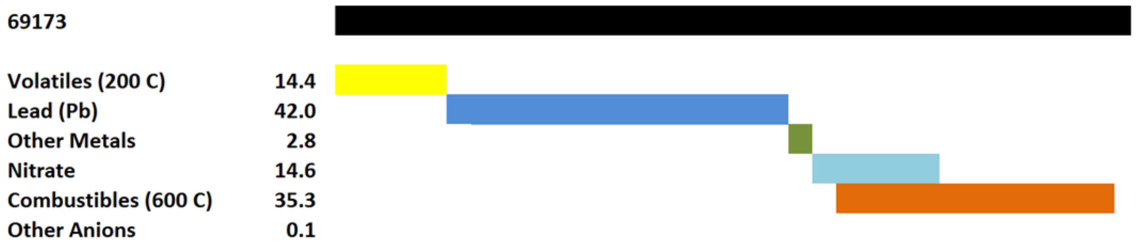
Isotope	atom%	
^{238}Pu	0.0201	
^{239}Pu	93.1330	
^{240}Pu	6.1306	
^{241}Pu	0.0688	
^{242}Pu	0.6475	
Pu Total	96	µg / g

Drum S851436, overpack 69173

Contained 4 gallons of free liquid, pH 0.
Processed January, 2014
Daughters: 69043, 69192, 69194

Sampled 7/8/2014
20.23 g solid collected
Appearance: Heterogeneous, red-brown and off-white, free-flowing solid.

Composition Profile[1]



Metals[2]

Lead (Pb, total)	42.0	wt%
Sodium (Na)	1.39	
Magnesium (Mg)	0.74	
Aluminum (Al)	0.38	
Calcium (Ca)	0.16	
Antimony (Sb)	11	µg/g
Beryllium (Be)	<0.3	
Bismuth (Bi)	48	
Boron (B)	12	
Cadmium (Cd)	< 3	
Copper (Cu)	< 8	
Gallium (Ga)	190	
Iron (Fe)	530	
Manganese (Mn)	<1	
Molybdenum (Mo)	5	
Nickel (Ni)	30	
Potassium (K)	65	
Silicon (Si)	63	
Thallium (Tl)	97	
Uranium (U)	310	
Yttrium (Y)	4	
Zinc (Zn)	< 11	

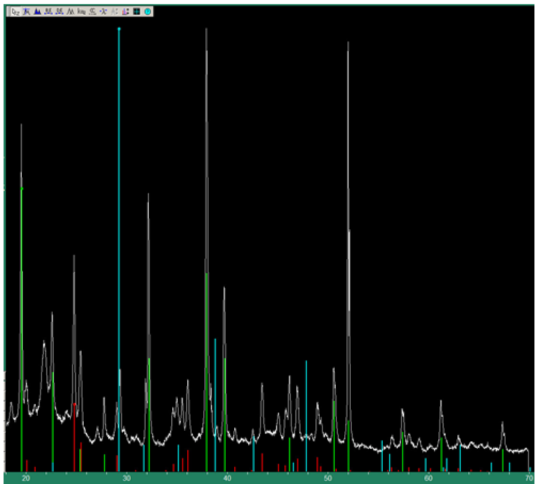
Non-Metals[3]

pH of absorbed liquid	1.7	
Available H^+ in solid	0.69	mol/kg
Volatiles (200 ^oC)	14.4	wt%
Combustibles (600 ^oC)	35.3	wt%
Nitrate (NO_3^-)	14.6	
Non-nitrate combustibles	22.8	
Carbon (C)	9.9	
(43 wt% of non-nitrate combustibles)		
Other anions		
Nitrite (NO_2^-)	70	µg/g
Fluoride (F^-)	150	
Chloride (Cl^-)	200	
Oxalate (free, $C_2O_4^{2-}$)	740	

Drum S851436, overpack 69173

Direct Solids Characterization

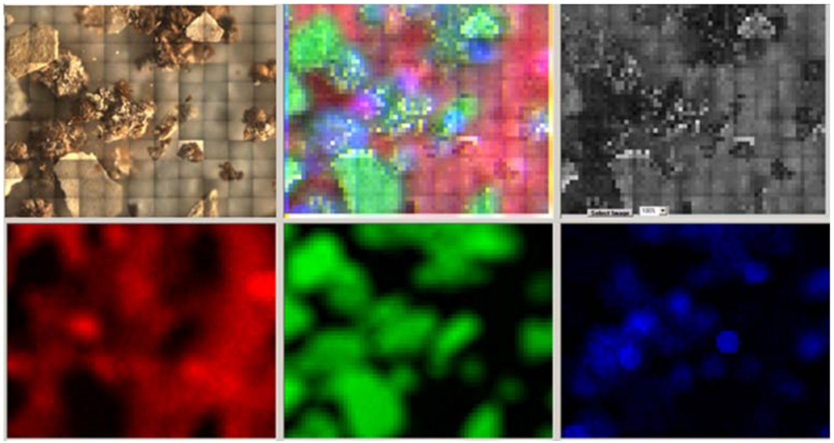
Powder X-ray Diffraction
(0-70 degrees plotted)



Confirmed:
Lead nitrate, $Pb(NO_3)_2$
Sodium nitrate, $NaNO_3$
Lead carbonate, $PbCO_3$

Not observed, or low confidence: Mg, Ca nitrates or oxalates; Iron oxide; Lead oxide; Lead oxalate

Micro X-ray Fluorescence
(25.1 mm x 19.6 mm area imaged)



Top row (L-R):

13. Visible light image
14. Composite of images 3-5
15. Greyscale

Bottom row (L-R):

16. Compton scatter (low-Z)
17. Lead (Pb)
18. Iron (Fe)

Also detected: Ca, Cr, Cu, K, Ni, U, and Pu.

Radionuclides[5]

Non-Destructive Screening

Isotope	µg / g	RSD
^{238}Pu	--	
^{239}Pu	6.95e+01	(4.6%)
^{240}Pu	--	
^{241}Pu	5.42e-02	(28%)
^{241}Am	9.52e+00	(4.1%)
^{243}Am	3.20e-02	(3.8%)
^{237}Np	3.60e-01	(4.3%)
^{235}U	1.68e+01	(11%)
^{238}U	--	

Destructive Analysis: Plutonium

Isotope	atom% (1)	atom% (2)
^{238}Pu	0.0214	0.0157
^{239}Pu	93.2753	93.7464
^{240}Pu	6.1771	6.1024
^{241}Pu	0.0883	0.0788
^{242}Pu	0.4379	0.0567
Pu Total	41	µg / g

Decay Heat 0.7 mW/kg solid (2%)

Appendix: Analytical Methods and Key Observations

General information: Analytical Characterization was performed by the Actinide Analytical Chemistry Group (C-AAC), Nuclear Materials Science Group (MST-16), and Advanced Nuclear Technology Group (NEN-2). Samples are identified by their Parent Drum ID# and Overpack Drum ID#. Key information recorded during parent drum remediation is provided, along with details of the solid samples collected from the emptied parent drum in 2014. A photo of each sample is also included, to provide a visual reference for the heterogeneity and texture of each material.

1. Composition Profile

The composition profile is a summary view of the % abundance by mass of the major constituents of each sample. *Volatiles* represents all weight loss occurring below 200 ^{o}C, including evaporation of water, nitric acid, and oxalic acid. *Lead* and *Other Metals* are the constituents reported in the Metals section of the report. *Nitrate* is the mass % of nitrate ion as determined by ion chromatography analysis. *Combustibles* represents all weight loss occurring between 200-600 ^{o}C, including combustion of polymers, and decomposition of metal oxalates and nitrates. The bar representing combustibles overlaps with the nitrate fraction, because metal nitrate salts typically decompose to oxides at the upper portion of this temperature regime. *Other Anions* represents the sum of all other water-soluble anions measured in the sample; any contributions from metal oxides were not directly measured are not included in the composition profile.

2. Metals

Metals were determined by destructive analysis using inductively-coupled plasma atomic emissions spectroscopy (ICP-AES) and mass spectrometry (ICP-MS). After thermolysis at 200 ^{o}C, duplicate solid samples were digested using concentrated nitric acid, with concentrated H_2O_2 added dropwise to break down the brown particulates. The resulting turbid, light yellow solutions were further heated to 130 ^{o}C for 50 hours in sealed Teflon vessels. A significant quantity of white crystals re-precipitated from the digestion solution; these were collected by filtration, dried, and weighed. X-ray fluorescence and x-ray diffraction analysis identified these crystals as $Pb(NO_3)_2$, which has very low solubility in concentrated nitric acid. The filtrates were serially diluted and analyzed for trace elemental constituents by ICP-AES and ICP-MS. Lead, and the major process elements Na, Mg, Al, and Ca, are reported as elemental mass % relative to the as-received solid; the reported Pb value is the sum of dissolved and insoluble lead. All other metals, regardless of levels, are reported in units of micrograms per gram of as-received solid. Estimated uncertainty on all reported values is +/-20%.

3. Non-Metals

Acidity of the solids was measured by leaching the as-received solids with DI water for 1 hour at room temperature, then analyzing the solution $[H^+]$ by titration with NaOH. This result is expressed in two ways. *pH of absorbed liquid* represents the predicted pH value that would be observed if the absorbed/interstitial water in each sample (as measured by 110 ^{o}C weight loss) could be separated from the sample. *Available H^+ in solid* represents the free H^+ concentration relative to the overall sample mass, including salts; the unit mol/kg is akin to solution molality.

As noted above, *Volatiles* represents the mass loss after the as-received solid was heated in air for 15 hours at 200 ^{o}C. *Combustibles* represents the additional mass loss after the 200 ^{o}C material was heated in air for an additional 1 hour at 600 ^{o}C. These temperature regimes correspond roughly to the evaporation of water and acids (<200 ^{o}C) and the decomposition of complex anions and polymers (200-600 ^{o}C).

Nitrate and *Other anions* were determined by anion chromatography, following the water leach of the as-received solid. *Nitrite* (NO_2^-) was measured using a sample leached at room temperature, to prevent its decomposition. All other anions were measured after leaching with water at 100 ^oC and serial dilutions. The anion chromatography result for *Oxalate* includes only "free" or lightly complexed oxalic acid that is soluble and exchangeable on an anion exchange resin; insoluble and strongly complexed oxalic acid is not detected by this method. The NO_3^- concentrations in 69139, 68492, and 68645 are stoichiometric with the Na^+ plus Pb^{2+} concentrations, to within about 10%, while sample 69173 is deficient in nitrate, and may instead be present as oxide, oxalate or other salt.

Carbon was determined by combustion analysis, using material that had been dried at 200 ^oC for 15 hours and then homogenized by grinding. Metal oxalate salts were used as matrix-matched analysis standards. The reported results are normalized to the as-received solid. Non-nitrate combustibles and %C of non-nitrate combustibles are calculated values. Values for %C in selected organic materials are provided here for reference.

Polystyrene, polyethylene, polypropylene:	85-92%
Cellulose, carbohydrates	40-45%
Poly(vinyl chloride)	38%
Oxalic acid	27%
Poly(vinylidene chloride) (Saran)	25%

4. Direct Solids Characterization

Powder X-Ray Diffraction specimens were dried at 200 ^oC for 15 hours and crushed into powder. Mounting for XRD analysis was done on glass slides, which were wrapped in polymer film to seal in radioactive contamination. All samples contained significant amounts of amorphous material. The diffraction peaks were compared to spectral libraries for the following classes of compounds: nitrates and oxalates of Na, K, Ca, Mg, Al, and Pb; oxides of Pb, Fe; and other simple salts of the above elements. Definitive identification was made for $NaNO_3$ and $Pb(NO_3)_2$ in all samples. The specimens contained varying ratios of $Pb(NO3)_2$ to $NaNO_3$, decreasing in the order 69173 > 68645 > 68492 > 69139, with an order of magnitude variation across the series. The corresponding mass concentrations of elemental Pb:Na determined by ICP-AES are 30.2 (69173); 10.5 (68645); 7.95 (68942); and 6.51 (69139). Following identification of $PbCO_3$ in sample 69173, an attempt at peak matching this compound was made for the other samples (red markers), but was not definitive. $PbCO_3$ is unlikely to be an original constituent of the acidic as-received sample, but may have originated with the thermal treatment.

Micro X-Ray Fluorescence samples were prepared after thermal treatment at 110 ^oC. To preserve the characteristics of the particles, no attempt was made to homogenize the material before mounting. The lower spatial resolution imaging reported in this summary was acquired using either a 1 mm or 2 mm beam-restricting aperture to cover a large spatial area. High spatial resolution data were also acquired using a polycapillary optic producing a 30 micron diameter X-ray beam (at Mo Kα energy); these are described in a separate report. The instrument uses a 50 W rhodium X-ray anode and a 30 mm^2 silicon drift detector. X-ray source filters were used to improve the signal-to-background ratios. Samples were contained using a Mylar film and supported by a cotton backer pad; very low atomic number elements (H through Mg) could not be detected in this configuration, due to absorption of their relatively low energy fluorescence x-rays. Most 3rd row elements (Al-Cl) are detectable in this configuration only if present at significant percent levels). The false-color images (bottom row) exhibit concentrated regions of light elements, lead, and iron, respectively. When compared to the visible light image, the three-color overlay (top center) suggests that the off-white flakes (e.g. in 69173) are lead compounds. Particles high in iron may be rust, and particles high in low-*Z* elements may be sodium nitrate.

5. Radionuclides

Non-Destructive Screening isotopic results were obtained by γ-ray spectrometry on the entire sample, as-received in its screw-cap plastic container. Samples were counted for 4 to 15 hours on an Ortec GMX40P co-axial HPGe detector with a relative efficiency of ~45%. Counting geometry and efficiencies were modeled in SNAP and FRAM codes, with approximate measured values of lead included as the matrix material. Isotopic content per g of sample was determined using SNAP output, divided by net sample mass. %RSD is for counting statistics only. Due to the high heterogeneity of the samples, and (in the case of 68645) the clumped appearance, the SNAP geometry simulations are not expected to provide accurate absolute results, but the ratios of nuclides within a sample are valid to within the documented uncertainties. Decay heat was calculated from the FRAM Specific Power (W/g Pu) and the IDMS total Pu result (below).

Destructive Analysis isotopic and total Pu results were obtained by Isotope Dilution Thermal Ionization Mass Spectrometry (IDMS) analysis of solutions prepared for Metals analysis (section 2, above). Duplicate dissolutions were spiked with an isotope dilution tracer prepared from NBS Standard Reference Material 996 (^{244}Pu) and calibrated against NBL CRM 126a, and the Pu was separated by anion exchange chromatography; the high uranium content in the samples necessitated extra column washes. For replicate analyses of a single sample (e.g. CRM 126a), the *Pu Isotopics* method uncertainty is typically 0.01-0.10 %RSD for major isotopes and 1-10% for minor and trace isotopes run by total evaporation. In all samples except 69173, the isotopic ratios in duplicate dissolutions agreed to within these uncertainties, and only one set of values is reported. Sample 69173 showed non-repeatable isotopic ratios that could not be explained by method uncertainty; both results are reported. Sample 69173-1 isotopics are consistent with mixing of a very small quantity of ^{242}Pu (of enrichment between 75-90%) into the more typical weapons-grade isotopics of sample 69173-2. Similarly, the elevated atom% of ^{238}Pu and ^{242}Pu in sample 68492 are consistent with mixing of a ^{242}Pu source with weapons-grade Pu. *Total Pu* content varied in replicate dissolutions by up to 6%.