Thermoanalytical investigation of the reactions causing the transuranic waste drum
breach that occurred in the Waste Isolation Pilot Plant

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Abstract:¹

In February 2014, an energetic gas-producing chemical reaction occurred in remediated plutonium processing waste emplaced in the Waste Isolation Pilot Plant causing the drum's seal to fail and release radioactive material into and outside of the plant. This article provides results of our probative study using simultaneous thermogravimetric and differential thermal analysis and accelerating rate calorimetry to determine the thermal sensitivities of selected simulated characteristic remediated wastes such as hydrogen- and hydrogen, metal-triethanolamine nitrates and nitric acid solidified and stabilized with wheat-based pet litter. These studies found that these nitrate wastes were chemically unstable and susceptible to gas-producing thermal runaway reactions. If undried or partially dried, self-sustaining or accelerating-exothermic reactions were delayed in nitrate- and organic-containing materials to above 100°C while air-dried nitric acid and pet litter began self-heating exothermic reactions near 30°C that led to thermal runaway. Caution must be exercised when managing nitrate-containing wastes.

Keywords: Waste Reactivity; Solidification and Stabilization; Plutonium Waste Management; Inorganic Nitrate Waste; Triethanolamine; Waste Isolation Pilot Plant drum breach; Nitrate-Organic Reactivity

1. Introduction

On February 14, 2014, a transuranic (TRU) waste drum emplaced in the salt mine at the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico, breached due to an internal chemical reaction [1]; Figure 1 provides a picture of the breached drum. The breach released radioactive material internal and external to WIPP. The breach occurred 72 days after the TRU waste drum was generated by Los Alamos National

¹ Abbreviations: accelerating rate calorimeter (ARC), Center for Chemical Process Safety (CCPS), Spilfyter[®] Kolorsafe[®] Acid Neutralizer (Kolorsafe), metal (M), melting point (mp), ambient relative humidity (RH), sWheat Scoop[®] (sWheat), triethanolamine (TEA), triethanolamine nitrate (TEAN), thermogravimetric and differential thermal analyzer (TG/DTA), transuranic (TRU), Waste Isolation Pilot Plant (WIPP).

Laboratory and 16 days after the drum was emplaced in Room 7 of Panel 7 of WIPP [2].

Unfortunately, the WIPP event was not unique for TRU wastes. In 2003 a fire occurred in a glovebox containing ceric nitrate/nitric acid/cloth decontamination wastes at the Rocky Flats Environmental Site [3, 4]. Because of the Rocky Flats fire, management at the Plutonium Finishing Plant on the U.S. Department of Energy (DOE) Hanford Site developed a plan for managing the nitrate-containing wastes that would arise from decontamination of its plutonium-contaminated gloveboxes based on experimental studies to determine the thermal stabilities of wastes arising from the candidate decontamination methods [5-9].

Figure 1. WIPP drum after breach

The TRU waste in the breached drum originated from plutonium recovery and purification operations at Los Alamos National Laboratory. The acidic residues from plutonium processing were evaporated and cooled to produce crystalline salts, which were collected, briefly rinsed with nitric acid, placed in plastic bags, and stored for about 30 years in lead-lined steel drums. After storage, Los Alamos National Laboratory 1) retrieved and opened the drums; 2) decanted, neutralized, and absorbed any separated free liquid; and 3) recovered and mixed the moist solids with an absorbent to sorb any interstitial liquid. The remediated waste was then placed into

TRU waste drums and sent to WIPP. The breached drum contained both remediated salt and liquid wastes.

During the campaign to remediate the wastes, the recovered nitrate salt and nitric acid solution was neutralized with Spilfyter[®] Kolorsafe[®] Acid Neutralizer [10], which is an aqueous triethanolamine (TEA) solution with alizarin pH indicator, and then solidified using the wheat-based pet litter unscented sWheat Scoop[®] (sWheat) [11]. The remaining nitrate salt portion was then treated with sWheat to absorb the interstitial acidic nitric acid/nitrate salt solution.

Treatment of the decanted acidic nitrate salt solution with the Lewis base TEA produced hydrogen triethanolamine nitrate (HTEAN) and mixtures of hydrogen and metal triethanolamine nitrate complexes (H,M)TEAN. TEA is a mildly alkaline [12, 13], polyfunctional ligand capable of bonding through its nitrogen and/or oxygen atoms to form complexes with Lewis acids including metal ions [14-16] to form nitrate salts (TEAN). The use of TEA to neutralize the acid added to the chemical complexity of the remediated waste by increasing the fuel loading and adding thermally sensitive reactive compounds composed of both an oxidant and fuel.

The TRU waste in the breached drum was a complex mixture of nitric acid, various metal nitrate salts, hydrogen and metallic ion TEA nitrates, and sWheat. This combination of oxidizing nitrate salt residues, organic sorbent, and neutralizing agent formed potentially incompatible reactive chemical mixtures based on guidance from the Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers [17, 18].

Other waste added to the drum included glovebox refuse, such as plastic bags and empty plastic bottles, and a glovebox glove reported to be lined with a mixture of bismuth, tungsten, and lanthanum. Clark and Funk [19] and Wilson et. al. [1] provide

detailed, in-depth descriptions of the original and remediated wastes that were put into the drum that breached.

To determine the feasibility of the particular mechanism(s) and chemical reactions that caused the waste drum to breach and release radioactive material into and outside of WIPP [2], the U.S. Department of Energy (DOE) assembled the WIPP Technical Advisory Team (TAT) [1] from selected national laboratories.

This article provides results from our probative set of thermoanalytical experiments performed in support of the Technical Advisory Team's assessment to identify the internal waste reaction(s) that under WIPP conditions could have led to the drum breach and radionuclides release. Using CCPS recommendations [17, 18] and our previous experience investigating reaction thermal sensitivities of 1) cellulose and different nitrate salt mixtures [5, 6, 8, 20, 21] and 2) amine-based complexants and nitrate mixtures [22] as our investigative foundation, we used simultaneous thermogravimetric and differential thermal analysis (TG/DTA) and accelerating rate calorimetry (ARC) to determine the thermal sensitivities of a selected set of waste constituents, simulated remediation products, and simulated remediation wastes. The simulant compositions were based on the multi-component composition of the mixture of the original Los Alamos liquid and salt TRU waste, remedial additives, and other materials that were put into the drum.

2. Experimental

Using concentration estimates from Wilson et al. [1] and Clark and Funk [23], and based on our own experience during testing with required sWheat treatment levels, the individual waste constituents and partially simulated wastes tested were

- sWheat,
- 1 volume part 3.5 M HNO₃ and 3 volume parts sWheat mixtures,

- HTEAN, (H,Pb)TEAN, and (H,Pb,Fe)TEAN complex salts produced from neutralization with TEA to pH paper-measured pH 7 of nitric acid and nitric acid solutions saturated with lead and iron nitrates, and
- HTEAN, (H,Pb)TEAN, and (H,Pb,Fe)TEAN solutions and salts mixed with sWheat.

A significant challenge for determining the thermal stabilities and sensitivities of wastes arising from aqueous processes is accurately determining the water or volatiles content as a function of time after assembly, given the design of the drum and susceptibility of the plastics used to contain the remediated wastes. A TRU waste drum is passively ventilated through a NucFil[®] filter [24] to ensure that hydrogen and other gases generated by radiolysis do not accumulate and create a hydrogen explosion or drum pressurization hazard. Our prior experience with TRU cloth decontamination wastes from Hanford's Plutonium Finishing Plant indicates that any water disposed in horse-tailed vented robust polyvinyl chloride plastic bags would evaporate, leaving dry waste. Water is particularly important because of its substantial heat capacity ($C_p = 4.179 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ at 298°C) and heat of evaporation (2.27 kJ g^{-1}) [25] between room temperature and 100°C , which will significantly influence whether exothermic reactions can self-propagate to ignition or thermal runaway. To assess the importance of water, we also evaluated the thermal reactivity of mixtures having reduced water content by using a variety of drying approaches, which are described in the preparation and results sections. It should be noted that the salt mine's desiccating qualities could contribute to drying the waste.

2.1. *Instruments*

A Seiko 5200 TG/DTA was used. The TG/DTA was temperature calibrated using melting point (mp) standards of 99.999% pure In (mp 156.6°C), Sn (mp 231.9°C), Zn

(mp 419.6°C), and 99.995% Pb (mp 327.5°C), and the instrument's four-point polynomial temperature calibration fit. The resulting calibration yielded a measured In mp of 155°C and Pb mp of 332°C. In general, the DTA results were baseline-corrected by the instrument. No mass calibration was performed, so TG results are reported as percentage of reported initial mass. The TG/DTA experiments typically used a heating rate of 5°C/min, either open aluminum or gold sample pans, and either static room air or an ultra-high purity Ar purge. The TG/DTA was located in a fume hood on a massive marble slab to minimize disruptive vibrations.

We used a Thermal Hazard Technology ARC, an adiabatic calorimeter that measures exothermic-reaction-driven sample self-heating [26, 27] up to 15°C/min; heating rates above 15°C/min underestimate the true rate. We used 2.5- to 8-g samples in 9.5-mL nominal 8.5-g titanium spherical sample containers capable of containing 20 MPa (200 bar). The ARC was calibrated through a single run with an empty sample container to ensure that the thermocouples reported equivalent temperatures. After calibration, the ARC's temperature drift was measured in one or more runs.

We operated the ARC in a heat/wait/search mode using a $> 0.01^\circ\text{C}/\text{min}$ self-heating exotherm criterion with the sample thermocouple located on the container's bottom pole. If the ARC does not observe an exothermic reaction, the instrument does not report any self-heating or pressure data, which for these tests led to gaps between non-sustainable exotherms.

Because of the test material's changing chemical and physical nature as the reaction(s) proceeds, we report the measured self-heat rate rather than adjusting the self-heat rate for the sample container's thermal inertia using the initial Φ -factor provided in Equation 1 [17]. The C_p values that could be used to calculate the initial

Φ -factor are $3.289 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ [28] for 3.5 M HNO_3 and its TEA-neutralized solutions, $0.524 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ [25] for the titanium bomb, and $1.63 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ [29] for sWheat.

provides the sample compositions and initial Φ -factor used for ARC testing, assuming that any mass loss during drying was simply water.

$$\Phi = 1 + (C_{p(bomb)} \times m_{bomb}) / (C_{p(sample)} \times m_{sample}) \quad [17] \quad (1)$$

Table I. Samples used in ARC Testing

Sample	Figure	Sample 3.5 M HNO_3 , g	(H,M)TEAN, g	sWheat, g	Ti Bomb, g	Sample Mass, g	Initial Φ - Factor
Undried HNO_3 /sWheat	Figure 6	1.136	NA	1.6656	8.5026	2.7855	1.696
7-Day Dried HNO_3 /sWheat	Figure 7	1.0483	NA	5.9113	8.4908	6.9596	1.340
Semi-dried (H,Pb,Fe)TEAN	Figure 12	NA	3.3538	NA	8.4411	3.3538	1.39
Undried HTEAN/sWheat	Figure 14	NA	1.124	1.654	8.4411	2.778	1.692
Undried (H,Pb)TEAN/sWheat	Figure 15	NA	1.1133	1.6722	8.5232	2.7855	1.699
Dried (H,Pb,Fe)TEAN/sWheat	Figure 17	NA	3.3653	5.6349	8.5	9.0002	1.220

2.2. Materials

The TEA used was Kolorsafe, supplied by NPS Corporation (Lot #14230).

Kolorsafe is a pH 10.2 aqueous solution containing 52.954 wt% TEA (3.87 M TEA)

and a pH indicator alizarin [10, 30]. Pet Care Systems, Inc. produced the sWheat,

which was derived from the whole grain of wheat [11, 31]. The 3.5 M HNO_3 was

prepared from Fisher Scientific *trace metal grade* concentrated HNO_3 (Lot #111302)

and deionized water. The $\text{Pb}(\text{NO}_3)_2$ used to prepare the $\text{Pb}(\text{NO}_3)_2$ -saturated 3.5 M

HNO_3 was Baker Analyzed ACS reagent grade (Lot #82050); based on Ferris [32],

the saturated $[\text{Pb}(\text{NO}_3)_2]$ concentration in 3.5 M HNO_3 is 0.3 M. The combination

$\text{Pb}(\text{NO}_3)_2$ - and Fe-saturated HNO_3 solution was prepared by treating Johnson Matthey

Electronics grade 99.2%, -48 mesh iron metal (Fe) powder (Lot #F17B15) with the prepared $\text{Pb}(\text{NO}_3)_2$ -saturated 3.5 M HNO_3 .

2.2.1. Preparation of Simulated Waste Solutions and TEANs

We prepared the tested simulated remediated liquid waste components by neutralizing solutions of 3.5 M HNO_3 , $\text{Pb}(\text{NO}_3)_2$ -saturated 3.5 M HNO_3 , and $\text{Pb}(\text{NO}_3)_2$ - and Fe-saturated HNO_3 to pH 7 with TEA to prepare solutions or slurries of HTEAN, (H,Pb)TEAN, and (H,Pb,Fe)TEAN. The pH was determined with pH paper. Neutralization produced solutions from 3.5 M HNO_3 and Pb-saturated HNO_3 , and solids from the (Pb,Fe)-saturated HNO_3 .

To determine the amount of TEA required for neutralization, the solutions of 3.5 M HNO_3 and $\text{Pb}(\text{NO}_3)_2$ -saturated 3.5 M HNO_3 were titrated with TEA. The 3.5 M HNO_3 had an equivalence point at approximately pH 4, indicating a concentration of the active TEA ingredient of 3.1 meq/mL Kolersafe compared to NPS's reported 3.8 M TEA [30]. The $\text{Pb}(\text{NO}_3)_2$ -saturated HNO_3 had only two equivalence points, one at pH 2.5 and the other at pH 5.5. Since achieving pH 7 requires additional TEA after equivalence, the neutralized liquid wastes would be expected to contain HTEAN, (H,M)TEAN, and free TEA.

2.2.2. Preparation of sWheat Mixtures

To prepare the sWheat mixtures, 3 volumes of sWheat were mixed with 1 volume of the Kolersafe-neutralized solutions [19], unneutralized 3.5 M HNO_3 , and (H,Pb)(NO_3)_{4.1} to produce the five mixtures: 1) HTEAN/sWheat, 2) (H,Pb)TEAN/sWheat, 3) (H,Pb,Fe)TEAN/sWheat, 4) 3.5 M HNO_3 /sWheat, and 5) (H,Pb)NO₃/sWheat. The latter two simulate the waste that would arise as a result of residual interstitial liquids in the salt fraction. Early testing of TEA-neutralized

surrogate liquid wastes used as-received sWheat and later testing used sWheat ground with a bladed electric coffee grinder (Figure 2).

Figure 2. Picture of as-received (left) and ground sWheat (right)

We used a variety of methods to prepare and dry the sWheat and liquid mixtures. Initially, the test mixtures were prepared inside the sample container. For the TG/DTA testing, the sample was dried at room temperature in flowing dry Ar. The method for drying the ARC samples evolved, starting with drying in the small diameter necked sample container using vacuum or Ar atmospheres and/or elevated temperature combinations.

Simple passive air drying in the laboratory at room temperature at ambient relative humidities (RHs) proved to be most effective at producing a final water content low enough to not quench room-temperature self-accelerating reactions. The 3.5 M HNO_3 /sWheat composed of 33.8% H_2O , 7.6% HNO_3 , and 59.6% sWheat lost 30% of its mass after 7 days of sitting in a laboratory at room temperature (16°C to 18.5°C) at RHs ranging from 10% to 15%. Assuming no evaporation or reaction between the HNO_3 and sWheat, the 30% mass loss translated to 90% H_2O evaporation. With the

high water loss, the residual liquid in the sWheat should be highly concentrated in HNO_3 .

Passive air-drying caused the freshly wetted 3.5 M HNO_3 /sWheat mixture to shrink, compact, and produce an orange, very hard, non-friable material, as shown in Figure 3. The strong orange color suggests reaction between sWheat and HNO_3 . In comparison, (H,Pb,Fe)TEAN/sWheat similarly dried at 10% to 21% RHs dried to its equilibrium water content in about 80 h. These two sWheat drying profiles indicate that when fully exposed at room temperature to RHs ranging from 10% to 20%, waste/sWheat mixtures would dry to their equilibrium liquid content in 3 to 10 days.

Figure 3. Effects of drying for 7.2 days on 3:1 vol ratio mixture of 3.5 M HNO_3 and dried sWheat.

3. Results and Discussion

According to the CCPS, the chemical reactivity hazards of any chemical system depend on 1) the potential energy of any chemical reactions that can occur between constituents, 2) the rates of any potential reactions and/or their decompositions, and 3) the process equipment. For a reactive waste chemical system to be safe, the engineered system must be able to adequately exhaust any gases produced and dissipate any reaction heat to prevent temperatures from rising to the level where the chemical reaction rate(s) produce heat faster than the engineered system can dissipate the heat [17].

The important factors identified by the CCPS affecting chemical stability include temperature, the nature and concentrations of the reactants, the nature and concentrations of impurities or other compounds present, solvent, air when air-sensitive compounds are present, and confinement. Temperature controls the chemical reaction rate with a 10°C increase, in general, causing the reaction rate to increase by a factor between roughly 2 and 4. The reactants determine the susceptibility to reaction through their functional group(s), the possible potential energies, and the potential to produce gaseous products. Systems meriting consideration or designated as incompatible include mixtures of organics and oxidizers other than oxygen, such as nitrates and nitrites. Reaction rate at a given temperature is roughly proportional to the reactants' concentrations. Impurities can have catalytic effects by reducing the activation energy E_a , increasing reaction rate, and reducing onset temperatures. Solvents may serve as a facilitating conveyance for reactants, as diluents, and as heat sinks. Confinement may cause the reaction rate to increase due to pressure increases or by preventing reactive product gases from escaping so that they might participate in secondary reactions [17].

3.1. *Thermal Behavior of sWheat*

To identify the reactions of the nitrate waste constituents with sWheat, the baseline thermal behavior must be known. We used TG/DTA to characterize sWheat's thermal sensitivities.

Shewry et al. [33] and Sramkova, Gregova, and Sturdik [34] report that wheat kernels are composed by mass of 13% to 15% bran or outer shell, 80% to 85% endosperm, and 2% to 3% germ. The bran is a complex mix of cellulose, lignin, pentosans, and polymers based on xylose and arabinose, which are tightly bound to proteins. The endosperm is nominally 83% starch, 13% proteins and enzymes, 1.5%

fats, 1.5% dietary fibers, and 0.5% minerals. Starch and proteins are the predominant kernel constituents at 65% to 70% and 14%, respectively.

Pure cellulose, a major component of sWheat, exhibits a variety of thermal decomposition behaviors depending on whether the decomposition gases are prevented from escaping [35-41]. If confined or partially confined under anaerobic conditions, the decomposition of cellulose starts near 200°C and is exothermic [38, 41]. If unconfined under anaerobic conditions, the decomposition is endothermic [38-40]. When heated in air, cellulose burns exothermically above 310°C [42, 43].

The TG/DTA output in Figure 4 shows that undried sWheat heated in Ar at 5°C/min immediately began a 10% endothermic mass loss that was likely water evaporation given the water retention properties of sWheat [31], the affinity of glucosidic materials for water, and the molecular distribution of water across the glucose polymer [44]. Upon completion of this first reaction, the sWheat lost another 65% through a series of endothermic mass losses. In air, the same initial endothermic mass loss occurred, followed by a series of exothermic reactions that began near 150°C and resulted in little residual mass when heated to 520°C.

Figure 4. Thermal behavior of undried sWheat in Ar as measured by TG/DTA at 5°C/min

3.2. Thermal Behavior of 3.5 M HNO_3 /sWheat

The TG/DTA (Figure 5) found that 3.5 M HNO_3 /sWheat dried for 3 h at 20°C in flowing Ar immediately began the expected endothermic mass loss likely due to water and possibly HNO_3 evaporation. While still losing water, the HNO_3 and sWheat began a rapid exothermic reaction near 110°C, which continued to 140°C. This reaction was followed by a slower exothermic reaction that continued to 500°C.

Applying the CCPS's 100°C rule-of-thumb safety margin for TG/DTA [17], HNO_3 /sWheat mixtures are likely susceptible to room-temperature exothermic reactions, as confirmed by ARC-testing. Normally, if the TG/DTA results indicated that exothermic reactions occurred at operational temperatures, further testing using more sensitive methods such as ARC would then be conducted to further refine acceptable operating conditions.

Figure 5. TG/DTA-measured behavior of 3.5 M HNO₃/sWheat in Ar at 5°C/min. Sample dried 3 h at 20°C in flowing Ar.

Figure 6 illustrates how water as a significant heat sink affects reaction propagation. Undried HNO₃/sWheat began a self-sustaining exothermic reaction in the ARC immediately at 30°C that sustained itself until 35°C, whereupon the self-heat rate fell below the exotherm criteria. Raising the temperature to 50°C restarted a self-sustaining exothermic reaction that lasted to 90°C, at which point the liquid evaporation heat consumption rate again exceeded the heat production rate. It is important to recognize that the chemical reaction itself does not stop at a particular temperature, but instead continues until one or both of the reactants are consumed. Subsequent heating to 120°C initiated a self-heating reaction that accelerated to 160°C, after which the heat production rate slowed until the experiment was stopped at 190°C.

We postulate that the heat production rates for the initial and later short-lived exothermic reaction(s) between HNO₃ and sWheat were lower than the heat consumption rates for the endothermic evaporation of water ($\Delta H_{\text{vap}} = 40.66 \text{ kJ/mol}$) and nitric acid reactions. The dominance of the liquid evaporation reaction rates

caused the ARC-observed self-heating rate to drop below the exotherm criteria (self-heat rate of $0.01^{\circ}\text{C}/\text{min}$). The endothermic evaporation reactions will compete with the exothermic reactions until the liquids are completely converted to gases or the heat production rate exceeds that of the competing endothermic reactions. If the exothermic reaction is unable to overcome the competing endothermic reaction, gaps between observed exothermic events such as those that occur in Figure 6. This postulate is supported by experiments of dried materials discussed later.

Figure 6. ARC-measured exothermic behavior of 2.8 g undried 3.5 M HNO₃/sWheat

These ARC and TG/DTA experiments using undried 3.5 M/sWheat indicate that

- 1) HNO₃ and sWheat react exothermically near room temperature but the reactions are prevented from sustaining themselves by water evaporation and
- 2) that with drying over time the reactions can propagate. With respect to HNO₃/sWheat waste in a vented drum, these low-temperature reactions in combination with the desiccating conditions of the salt mine will accelerate the drying, eventually permitting self-accelerating reactions between HNO₃/sWheat, assuming ample reactants remain.

In contrast to undried mixtures, when allowed to dry open to 20°C air, the low-temperature exothermic reactions will self-heat the mixture to near 80°C, when thermal runaway or ignition occurs as shown in Figure 7 or by Scheele, Minette, McNamara and Schwantes [45]. In these two ARC experiments, self-sustaining and accelerating reactions began immediately at 40°C and 30°C, respectively. The samples slowly self-heated to 73°C and 78°C, whereupon thermal runaway reactions or ignition occurred, rupturing the spherical titanium containers (see Figure 7). For the 16-h dried mixture, the last measured self-heat rate, pressure, and pressure change rate reached 40°C/min, 12 bar, and 190 bar/min [45], respectively.

Figure 7. ARC-measured thermal behavior of 7.0 g of 7-day, air-dried saturated 3.5 M HNO₃/sWheat. Inset provides picture of ruptured container.

These two ARC experiments indicate that 3.5 M HNO₃/sWheat dried at room temperature will self-heat from room temperature to thermal runaway in a sealed system, and thus could explain the WIPP drum breach event. Some evaporative drying of the waste would be expected within a TRU waste drum since the drum is vented through a NucFil[®] drum vent filter and exposed to dry air [24].

3.3. Thermal Behavior of (0.3 M $\text{Pb}(\text{NO}_3)_2$ -3.5 M HNO_3)/sWheat

Other waste constituents, such as $\text{Pb}(\text{NO}_3)_2$ from dissolution of the original Pb shielding, could react directly with the sWheat or catalyze or otherwise affect the thermal sensitivities of reactions between HNO_3 and sWheat mixtures.

Comparison of Figure 8 with Figure 5 shows that an additional, lower-temperature exothermic reaction arises near 100°C (peak maximum 110°C) when 0.3 M $\text{Pb}(\text{NO}_3)_2$ was present in 3.5 M HNO_3 . The exothermic reaction observed for the neat 3.5 M HNO_3 with sWheat with a peak maximum of 130°C appears unchanged. This indicates that $\text{Pb}(\text{NO}_3)_2$ reacts with the sWheat at a lower temperature than pure HNO_3 , suggesting that the presence of Pb should make the mixture more thermally sensitive (lower onset temperature).

Figure 8. Thermal behavior of (H,Pb) NO_3 /sWheat in Ar as measured by TG/DTA at 5°C/min. Dried for 4 h at 20°C in Ar.

3.4. Thermal Behavior of Remediated Liquid Waste

The other major potentially reactive waste constituent in the WIPP drum that breached was the TEA-neutralized nitric acid solution sorbed onto sWheat. Metal complexes of TEA exhibit variable thermal stabilities, with some exhibiting

“explosive” properties when heated to elevated temperatures. Using DTA and TGA at a heating rate of 10°C/min, İçbudak, Yilmaz, and Olmez [46] found that the TEA nitrate salts of La, Ce(III), and Nd(II) decomposed “violently” in nitrogen. These decompositions began and ended at 198°C and 800°C, 195°C and 500°C, and 255°C and 600°C, respectively. The La salt decomposed to $\text{La}_5\text{O}_7\text{NO}_3$. The Ce(III) and Nd(II) salts decomposed in air to CeO_2 and Nd_2O_3 , with similar thermal behaviors.

HTEAN melts at 80°C and is reported to begin exothermic (heat-producing) decomposition with the release of gaseous products at 250°C to 325°C when heated at 175°C s⁻¹ under 1380 bar (1380 kPa) of Ar [47]. Gases released included CO_2 , N_2O , CO, NO, NH_3 , and HCN. The gaseous nitrogen oxides can react with the fuel constituents in the waste mixture and the nitrogen oxide oxidants can react with the fuel gases CO, NH_3 , and HCN. Thus, protonation of TEA to produce HTEAN results in a more thermally unstable chemical compound that will decompose violently, producing gases that could participate in secondary exothermic reactions.

3.4.1. Thermal behavior of HTEAN, (H,Pb)TEAN, (H,Pb,Fe)TEAN

The TG/DTA found that HTEAN dried at 40°C for 2 h in Ar begins to decompose exothermically starting near 220°C, as shown in Figure 9. Its decomposition was violently exothermic, as indicated by the rapid mass increase caused by the rapid production of gases, forcing the TG to register a very rapid mass increase and a subsequent ejection of sample.

Figure 9. Thermal behavior of HTEAN as measured by TG/DTA at 5°C/min in Ar. Dried at 35°C for 2 h in Ar.

In the TG/DTA experiment shown in Figure 10, the TEA-neutralized 0.3 M $\text{Pb}(\text{NO}_3)_2/3.5 \text{ M HNO}_3$ was prepared in the sample pan, dried in the TG/DTA for 5 min at 25°C, heated to 55°C at 10°C/min, and isothermally dried for 50 min. This (H,Pb)TEAN exhibited violent reactivity at high temperatures similar to HTEAN, but was accompanied by a series of additional, low-temperature exothermic mass loss reactions between 20°C and 40°C. The TG/DTA observed a series of exothermic reactions beginning near 230°C that culminated in a rapid exothermic mass loss and ejection starting at 240°C. Figure 11 provides a picture of the ejected (H,Pb)TEAN thermal decomposition product and sample pan which illustrates rapid gas production.

Figure 10. Thermal behavior of (H,Pb)TEAN as measured by TG/DTA 1) dried for 5 minutes at 25°C, 2) heated to 55°C at 10°C/min and dried for 50 min, and 3) heated at 5°C/min in Ar).

Figure 11. (H,Pb)TEAN thermal decomposition product

The (H,Pb,Fe)TEAN for the ARC test was prepared in two stages by adding near equal amounts of the TEAN solution to the ARC container. The first addition was dried for 3 days at 40°C and the second plus first addition was dried for two days at room temperature and then dried for 2 h at 40°C to 50°C in an Ar-dry box, but did not fully dry.

The ARC analysis of 3.4 g of dried (H,Pb,Fe)TEAN provided in Figure 12 shows that below 100°C, the ARC observed several unsustainable exotherms with self-

heating rates exceeding $0.01^{\circ}\text{C}/\text{min}$ after each 10°C step increase; however, immediately after identification of exothermic behavior, the self-heating rate fell to negative rates, resulting in only the pressure and pressure change rate being presented. The absence of observed, sustainable, low-temperature reactivity could be a result of the presence of volatile liquids. Once dry, a self-accelerating exothermic reaction began at 130°C and continued to 215°C , when the gas production and self-heating rate accelerated, leading to a ruptured container. The last recorded self-heat rate, pressure, and pressure change rate were $100^{\circ}\text{C}/\text{min}$, 210 bar, and $6000\text{ bar}/\text{min}$, respectively, which indicate a very energetic and fast gas-producing reaction.

Figure 12. ARC-measured exothermic behavior of 3.4 g semi-dried (H,Pb,Fe)TEAN prepared in two stages, with the first addition dried for 3 days at 40°C and the combined second and first dried 2 days at room temperature and 2 h at 40°C to 50°C in an Ar-dry box.

3.4.2. Reactivity of (H,M)TEAN/sWheat

After neutralization in the remediation process, the liquid fraction was solidified with sWheat. As shown in Figure 13, the TG/DTA of HTEAN/sWheat dried at 40°C in Ar found an exothermic mass loss between 95°C and 180°C , followed immediately by a second, more significant exothermic mass loss. When heated in air at $5^{\circ}\text{C}/\text{min}$ after

drying at 50°C in Ar, the HTEAN/sWheat had a small exothermic reaction between 60°C and 95°C, followed immediately by a weak exotherm to 180°C, which was followed by a series of significant exothermic mass loss reactions.

Figure 13. Thermal behavior of HTEAN/sWheat in Ar as measured by TG/DTA at 5°C/min. Sample dried at 40°C in Ar for 2 h.

The ARC found that undried HTEAN/sWheat began a self-accelerating exothermic reaction after being heated to 145°C (Figure 14). It is likely that the evaporation of water prevented the ARC from detecting the TG/DTA-observed HTEAN exothermic reactions below 100°C and the added thermal mass of sWheat delayed the onset of the 125°C HTEAN decomposition observed for (H,Pb,Fe)TEAN.

Figure 14. ARC-measured exothermic behavior of 2.8 g undried HTEAN/sWheat.

In contrast to undried HTEAN/sWheat, the ARC detected unsustainable exothermic reaction(s) for the same amount of (H,Pb)TEAN/sWheat near 35°C (Figure 15). This suggests that the addition of Pb heightens the thermal sensitivity of TEAN/sWheat. The significant self-accelerating reaction began near the same temperature of 145°C.

Figure 15. ARC-measured exothermic behavior of 2.8 g undried (H,Pb)TEAN/sWheat.

Comparison of Figure 8 and Figure 9 with Figure 16 shows that, in contrast to the neat hydrogen or metal TEANs, when mixed with the sWheat, the added thermal mass of sWheat prevents the TG/DTA-measured 220°C violent decomposition of the neat (H,M)TEANs. The oxidation of the sWheat with its significant DTA peak at 300°C confounds the interpretation of the TG/DTA analysis, but it is likely that the two sharp DTA peaks were due to TEAN decomposition.

Figure 16. TG/DTA-measured thermal behavior of partially dried (H,Pb,Fe)TEAN/sWheat in air at 10°C/min as function of time. Sample dried for 11 days at room temperature in air.

For a (H,Pb,Fe)TEAN mixture partially dried at 50°C for 5.5 h, the ARC observed several unsustainable, low-temperature exotherms below 125°C (Figure 17), followed by a self-accelerating reaction beginning at 125°C, which led to thermal runaway that ruptured the titanium sample container. The low-temperature reactions likely could not sustain themselves because the rate of heat production was less than the heat demands of water evaporation and heat dissipation of the sWheat. This low-temperature reactivity suggests that when dry this TEAN, if not others, will support low-temperature self-accelerating reactions similar to the HNO₃/sWheat. Additional testing of dried (H,M)TEANs and sWheat is needed to determine if these waste

constituents can sustain self-sustaining or accelerating reactions that are initiated near room temperature.

Figure 17. ARC-measured exothermic behavior of 9 g of (H,Pb,Fe)TEAN/sWheat dried at 50°C for 5.5 h in sample container.

4. Summary and Conclusions

Probative thermoanalytical studies investigating the reactivity of wheat-based pet litter mixed with acidic nitrates and/or hydrogen and metal complexes of TEA found that certain individual constituents and their mixtures are kinetically self-reactive at temperatures as low as room temperature. The room temperature-reactive dried mixtures self-heated under adiabatic and closed conditions to thermal runaway at 80°C. Upon thermal runaway, sample sizes of a few grams of a solid mixture produced gases sufficient to exceed pressures of 20 MPa (200 bar) and rupture a robust spherical reaction vessel fabricated from titanium metal. Water was found to quench and prevent self-propagation of low-temperature reactions. These results may help explain the cause of the drum breach in WIPP.

Specifically for the tested simulated waste constituents:

- A mixture of 3.5 M HNO_3 and sWheat, if dry, can self-heat beginning between 30°C and 40°C, and can self-heat under closed, adiabatic conditions to an 80°C energetic, rapid, gas-producing thermal runaway.
- Addition of lead nitrate to 3.5 M HNO_3 added an earlier initial onset reaction of nitrate with sWheat in TG/DTA testing, suggesting that metals in the waste can catalyze the reaction between nitrate and sWheat or other glucosodic materials.
- (H,M)TEANs begin to decompose (self-react) at temperatures between 125°C and 150°C, producing heat and gases, and eventually decompose violently at temperatures over 200°C in TG/DTA tests.
- Mixtures of (H,M)TEANs and sWheat have similar decomposition onsets, but did not decompose violently in TG/DTA tests. However, further testing of dried mixtures is required to confirm the lack of violent decomposition.
- The presence of free or bound water in all of the systems studied here significantly affected the propagation of reactions observed by the ARC at temperatures below 100°C.

Because of the limited scope and duration of our probative tests, these findings present an incomplete evaluation of the susceptibility of all possible Pu-waste constituents to low-temperature thermal initiation. Additionally, ARC testing is recommended for waste constituents that exhibit exothermic reactions observed below 100°C by TG/DTA to more accurately evaluate self-heating and reactivity. Specifically, we recommend ARC testing of dried (H,Pb,Fe)TEAN/sWheat, (H,M)TEAN, and (H,M)TEAN/sWheat. We also recommend testing using TG/DTA coupled with evolved gas analysis, ARC, and even larger-scale testing “cook-off” experiments to evaluate aging of remediated waste constituents.

The breach of the WIPP drum, the past accident at the Rocky Flats Environmental Site, studies on potential decontamination wastes from the Plutonium Finishing Plant, and these studies illustrate the reactivity hazards of mixing a strong oxidant with fuel(s) and emphasize the importance of ensuring that TRU and other industrial wastes containing oxidants and fuels are stable at all expected environmental conditions during generation, interim storage, and transport, and over time following emplacement in a disposal facility. To avoid potential reactivity hazards at DOE licensed nuclear disposal facilities, wheat-based pet litter should not be used to solidify and stabilize acidic nitrates. Our studies hint that the use of TEA commercially to neutralize nitric acid solutions of metal nitrate salts should be carefully considered, particularly if the wastes could dry.

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