Thermal Reactivities of Transuranic Wastes in the Breached Drum Emplaced in the Waste Isolation Pilot Plant

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Abstract:

In February 2014, a gas-producing chemical reaction occurred in transuranic waste emplaced in the Waste Isolation Pilot Plant in New Mexico that breached the drum's seal and released

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[1] Abbreviations: Center for Chemical Process Safety (CCPS), Los Alamos National Laboratory (LANL), Spilfyter® Kolorsafe® Acid Neutralizer (Kolorsafe), sWheat Scoop® (sWheat), Technical Advisory Team (TAT), Waste Isolation Pilot Plant (WIPP), triethanolamine nitrate (TEAN).

radioactive material into and outside of the plant. In a probative study, we investigated the thermal reactivities of selected simulated waste constituents. The tested waste constituents included triethanolamine-neutralized nitric acid/nitrate salt solutions solidified with wheat-based pet litter, triethanolamine nitrate salts, and nitric acid solidified with wheat-based pet litter. The undried or partially dried neutralized waste supported self-sustaining exothermic reactions after being heated to above 100°C, although unsustainable exothermic reactivity was observed near 40°C. The representative interstitial nitric acid and pet litter mixture air dried for 16 hours and 8 days began self-heating exothermic reactions at 30°C and 40°C that led to thermal runaways or ignition. These studies determined that these nitrate waste components solidified and stabilized with wheat-based pet litter were chemically unstable and could have initiated or contributed to the waste drum breach.

Keywords: Waste Isolation Pilot Plant drum breach, TRU waste stability, Nitric acid organic reactivity, Waste components compatibility, Organic nitrates thermal stability

1. Introduction

On February 14, 2014, a transuranic (TRU) waste drum in the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico, breached due to an internal chemical reaction [1]; see Figure 1. 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 Laboratory (LANL) and 16 days after the drum was emplaced in Room 7 of Panel 7 of WIPP [2].

Figure 1. Breached WIPP drum after breach

The TRU waste in the breached drum originated from plutonium recovery and purification operations. In general, 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, LANL retrieved and opened the drums, decanted and remediated any separated free liquid, and recovered and mixed the moist solids with an adsorbent to sorb any liquid. Any free liquid collected was neutralized and mixed with adsorbent. The remediated waste was then placed in TRU waste drums and sent to WIPP. The breached drum contained both remediated salt and liquid.

During the campaign to remediate the wastes, the recovered nitrate salt and nitric acid solution was neutralized with Spilfyter® Kolorsafe® Acid Neutralizer (Kolorsafe) [3], which is an aqueous triethanolamine (TEA) solution with alizarin pH indicator, and then solidified using the wheat-based pet litter unscented sWheat Scoop® (sWheat) [4]. 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 hydrogen and metal (M) triethanolamine nitrate complexes [(H,M)TEAN]. TEA is a mildly alkaline [5, 6], polyfunctional ligand capable of bonding through its nitrogen and/or oxygen atoms to form complexes with Lewis acids including metal ions [7-9] to form nitrate salts. The use of TEA to neutralize the acid added to the chemical complexity of the remediated waste by increasing the fuel loading and adding potentially 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, a variety triethanolamine nitrates, and sWheat. This combination of the oxidizing nitrate salt residues, organic sorbent, and neutralizing agent represent a set of a potentially incompatible chemical mixtures based on guidance from the Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers [10, 11].

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 [12] and Wilson et. al. [1] provide detailed, in-depth descriptions of the original and remediated wastes that were put into the drum that breached.

The DOE assembled the Technical Advisory Team (TAT) from selected national laboratories to determine, to the extent feasible, the particular mechanism(s) and chemical reactions that caused the waste drum to breach and release radioactive material into and from WIPP [2]. In support of the TAT's assessment, we performed a probative set of thermoanalytical experiments to identify the internal waste reaction that under WIPP conditions could have led to the drum breach.

Based on CCPS recommendations [10, 11] and previous studies investigating reaction thermal sensitivities of cellulose and different nitrate salt mixtures [13-17] and of amine-based complexants and nitrate mixtures [18], we used simultaneous thermogravimetric and differential thermal analysis and accelerating rate calorimetry to measure the thermal sensitivities of a selected set of simulated remediation products and simulated remediation wastes based on the multi-component composition of the mixture of original liquid and salt TRU-waste, remedial additives, and other materials that were put into the drum. This article provides the results of these probative experimental studies performed to identify a waste constituent susceptible to low-temperature-initiated self-sustaining reactions that could explain the breach of the drum.

2. Experimental

Using TAT [1] and Clark and Funk [19] concentration estimates and based on our own experience with required sWheat treatment levels, the individual waste constituents and partially simulated wastes tested were

- sWheat,
- 1 volume part 3.5 M HNO_3 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.

One of the significant challenges for determining the thermal stabilities and sensitivities of wastes arising from aqueous processes is accurately considering the water or volatiles content as a function of time after assembly. A TRU waste drum is passively ventilated through a NucFil® filter 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 Hanford's Plutonium Finishing Plant TRU cloth decontamination wastes 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 significant heat capacity ($C_p = 4.179$ J g^{-1} °C^{-1} at 298°C) and heat of evaporation (2.27 kJ g^{-1}) [20] between room temperature and 100°C, which will significantly influence whether exothermic reactions can self-propagate to ignition or thermal runaway. To evaluate the importance of water, we also evaluated the thermal reactivity of mixtures having reduced water content. We tried a variety of drying approaches, which are described in the preparation and results sections.

2.1. Instruments

A Seiko 5200 simultaneous thermogravimetric and differential thermal analyzer (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), and 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 Hazards Technology accelerating rate calorimeter (ARC), an adiabatic calorimeter which measures exothermic reaction driven sample self-heating [21, 22] up to 15°C/min. We used 2.5- to 8-g samples in 9.5-mL titanium spherical sample containers capable of containing 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°C/min self-heating exotherm criterion with the sample thermocouple located on the container's bottom pole. The reported self-heat rate is adjusted for the sample container's thermal inertia using the Φ-factor provided in Equation 1 [10]. The C_p values used were 3.289 J g^{-1} $°C^{-1}$ [23] for 3.5 M HNO_3 and its solutions, 0.524 J g^{-1} $°C^{-1}$ [20] for the titanium bomb, and 1.63 J g^{-1} $°C^{-1}$ [24] for sWheat.

$$\Phi = 1 + (C_{p(bomb)} \times m_{bomb})/(C_{p(sample)} \times m_{sample}) \text{ [10]} \qquad \textbf{(1)}$$

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 [3, 25]. Pet Care, Inc. produced the sWheat pet litter, which was derived from the whole grain of wheat [4, 26]. The 3.5 M HNO_3 was prepared from Fisher Scientific trace metal grade concentrated HNO_3 (Lot # 111302) and deionized water. The $Pb(NO_3)_2$ used to prepare the $Pb(NO_3)_2$-saturated 3.5 M HNO_3 was Baker Analyzed ACS reagent grade (Lot #82050); based on Ferris [27], the saturated $[Pb(NO_3)_2]$ concentration in 3.5 M HNO_3 is 0.3 M. The combination $Pb(NO_3)_2$- 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 $Pb(NO_3)_2$-saturated 3.5 M HNO_3.

2.2.1. Preparation of Simulated Waste Solutions and TEANs

To prepare the tested simulated remediated liquid waste components, solutions of 3.5 M HNO_3, $Pb(NO_3)_2$-saturated 3.5 M HNO_3, and $Pb(NO_3)_2$- and Fe-saturated HNO_3 were neutralized 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.

The solutions of 3.5 M HNO_3 and $Pb(NO_3)_2$-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 Kolorsafe compared to NPS's reported 3.8 M TEA [25]. The $Pb(NO_3)_2$-saturated HNO_3 had two equivalence points, one at pH 2.5 and the other at pH 5.5, with no other equivalence points found. 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. sWheat Mixture Preparations

To prepare the sWheat mixtures, 3 volumes of sWheat were mixed with 1 volume of the Kolorsafe-neutralized solutions [12], 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) $(H,Pb)NO_3$/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 ways to prepare and dry the sWheat and liquid mixtures. Initially, the test mixtures were prepared inside the sample holder. 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 a variety of 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 most effective with the final water content low enough to not quench room temperature self-propagating 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 8 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% of the H_2O evaporated. With the high water loss, the residual liquid in the sWheat should be highly concentrated in HNO_3.

Drying caused the 3.5 M HNO_3/sWheat mixture to shrink and compact and produce an orange, very hard, non-friable material. The strong orange color suggests reaction between sWheat and HNO_3. In comparison, (H,Pb,Fe)TEAN/sWheat dried similarly at RHs ranging from 10% to 21% and 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.

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 [10].

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 [10].

3.1. Thermal Behavior of sWheat

For reference purposes and with combustion of sWheat as a potential contributor to the breaching event, we used TG/DTA to determine the thermal behavior of sWheat under anaerobic and aerobic conditions. Shewry et al. [28] and Sramkova, Gregova, and Sturdik [29] 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 exhibits a variety of thermal decomposition behaviors depending on whether the decomposition gases are prevented from escaping [30-36]. If confined or partially confined under anaerobic conditions, the decomposition starting near 200°C is exothermic [33, 36]. If unconfined, the decomposition is endothermic [33-35]. When heated in air, cellulose burns exothermically above 310°C [37, 38].

As shown in Figure 3, when undried sWheat is heated in Ar at 5°C/min, it immediately begins an endothermic mass loss. Given the water retention properties of sWheat [26] and the affinity of glucosidic materials for water and the molecular distribution of water across the glucose polymer [39], this nominal 10% mass loss is likely water evaporation. Just as this first reaction completes, the sWheat begins to decompose through a series of endothermic mass losses, resulting in a relative 25% residual mass after being heated to 500°C. In air, the same initial endothermic mass loss occurs, followed by a series of exothermic reactions beginning near 150°C that result in little residual mass when heated to 520°C.

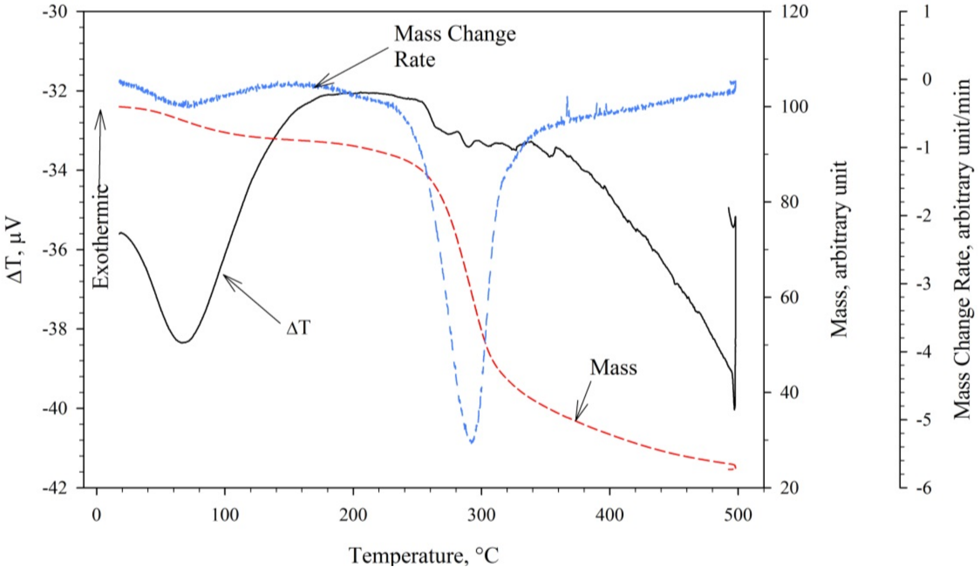

Figure 3. Thermal behavior of undried sWheat in Ar as measured by TG/DTA at 5°C/min.

3.2. Thermal Behavior of 3.5 M HNO_3/sWheat

When 3.5 M HNO_3/sWheat was dried for 3 h at 20°C in flowing Ar and then heated in the TG/DTA at 5°C/min in Ar, it immediately began the expected endothermic mass loss likely due to water and possibly HNO_3 evaporation (see Figure 4). As this sample continued to lose water, near 110°C the HNO_3 and sWheat began a rapid exothermic reaction, which continued to 140°C. A slower exothermic reaction continued until the experiment was stopped at 500°C. Applying the 100°C rule-of-thumb safety margin for TG/DTA [10], HNO_3/sWheat mixtures likely are susceptible to room-temperature exothermic reactions.

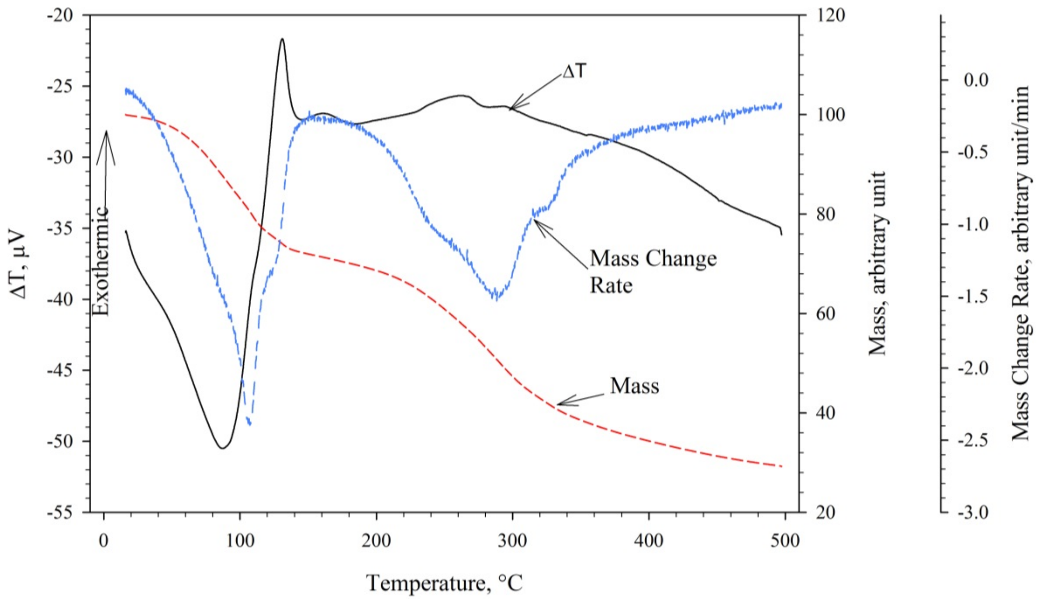

Figure 4. TG/DTA-measured thermal behavior of 3.5 M HNO_3/sWheat in Ar at 5°C/min. Sample dried 3 h at 20°C in flowing Ar.

In the ARC experiment of undried material (Figure 5), the ARC observed an exothermic reaction immediately after starting the experiment at 30°C that sustained itself until 35°C, whereupon the self-heat rate fell below the exotherm criteria. It is likely that the chemical reaction rate between the HNO_3 and sWheat (undried) was slower than the endothermic liquid evaporation rate, and could not produce sufficient heat to sustain itself at this temperature. Increasing the temperature to 50°C increased the reaction rate such that it was able to sustain itself to about 90°C in the presence of a lesser amount of volatiles. When endothermic demands of liquid evaporating again exceeded the heat production rate required for the sample to continue to self-heat, the ARC no longer observed exothermic behavior. It is important to recognize that the chemical reaction itself does not stop at a particular temperature until one or both of the reactants are gone. Upon heating to 120°C, the ARC detected a self-heating reaction that sustained itself to 160°C, where it slowed until the experiment ended at 190°C. This experiment, consistent with the TG/DTA results, indicates that there is an exothermic reaction between HNO_3 and sWheat near room temperature, but the 2.8-g sample could not sustain a heating rate of 0.01°C/min below 40°C in the presence of the volatile liquids in the sample.

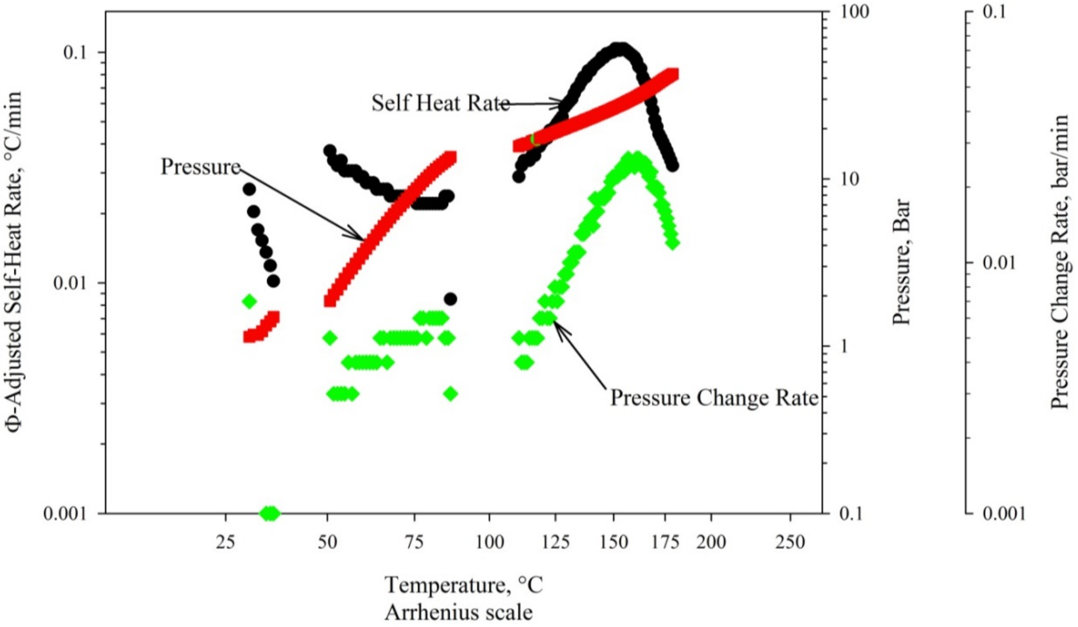

Figure 5. ARC-measured exothermic behavior of 2.8 g undried 3.5 M HNO_3/sWheat

This ARC experiment illustrates the importance of water's dampening effect on the ability of a reactive chemical system to support self-heating, particularly when compared to the ARC analysis of a sample dried for 8 days, which is discussed next. This ARC experiment also illustrates that, even in the presence of a significant heat sink like water, room temperature exothermic reactions are occurring that can accelerate the evaporation of water, which will shorten the time required for the waste to dry.

As shown in Figure 6, immediately upon starting the ARC experiment at 40°C, the 7.0 g of 8-day dried 3.5 M HNO_3/sWheat began a self-sustaining reaction that heated the sample to 73°C, after which a thermal runaway reaction began that ruptured the spherical titanium container, also shown in Figure 6. In another ARC experiment using 7.5 g of 3.5 M HNO_3/sWheat dried for 16 h in the open, a self-sustaining reaction began immediately upon starting the experiment at 30°C that continued to a thermal runaway or ignition at 80°C; the last measured self-heat rate, pressure, and pressure change rate reached 40°C/min, 12 bar, and 190 bar/min and the container also ruptured [40]. These two ARC experiments indicate that 3.5 M HNO_3/sWheat dried at room temperature will self-heat from room temperature to thermal runaway. 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 exposed to dry air [41].

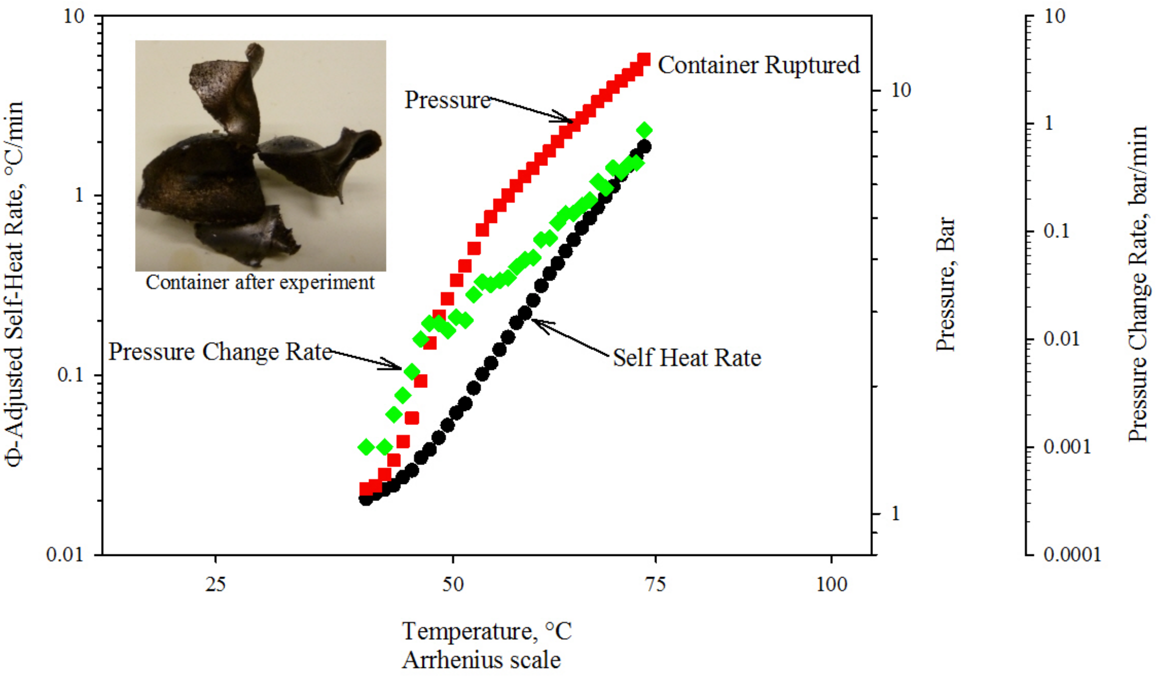

Figure 6. ARC-measured thermal behavior of 7.0 g of 8-day, air-dried saturated 3.5 M HNO_3/sWheat. Inset provides picture of ruptured container.

3.3. Thermal Behavior of 0.3 M $Pb(NO_3)_2$*-3/.5 M* HNO_3

As shown in Figure 7, the presence of 0.3 M $Pb(NO_3)_2$ in 3.5 M HNO_3 lowered the initial exothermic reaction temperature with sWheat to near 100°C but did not eliminate the exothermic reaction observed for the 3.5 M HNO_3 reaction with sWheat. This indicates that $Pb(NO_3)_2$ reacts with the sWheat at a lower temperature than HNO_3. No ARC tests were done to evaluate the effects of Pb or other solutes in the interstitial solution sorbed onto sWheat.

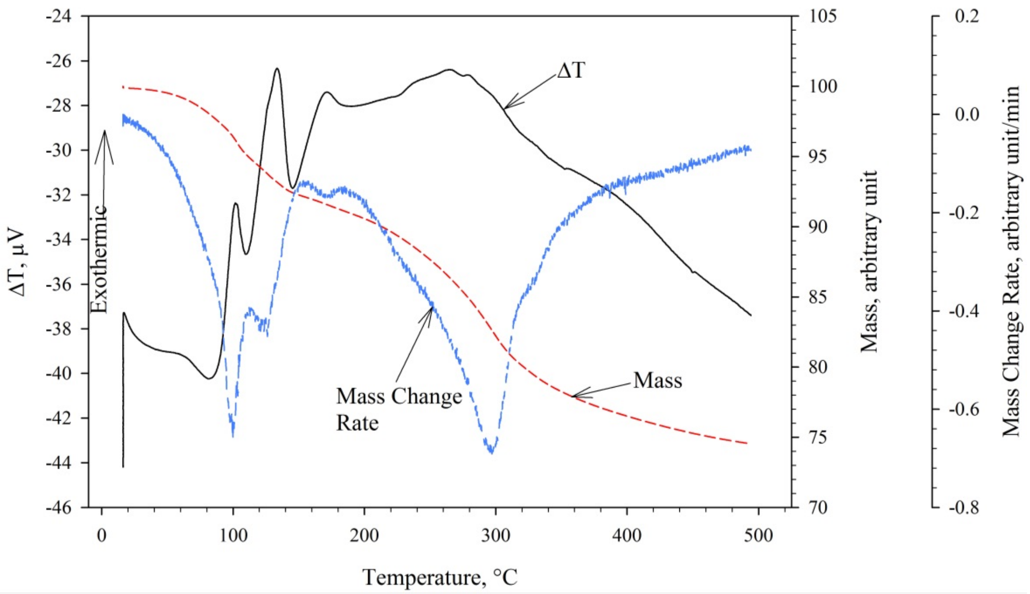

Figure 7. Thermal behavior of (H,Pb)NO_3/sWheat in Ar as measured by TG/DTA at 5°C/min. Dried for 4 h at 20°C in Ar.

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. We used TG/DTA and/or ARC to determine the thermal stabilities of the predominant neutralization product HTEAN, HTEAN/sWheat, partially dried (H,Pb)TEAN, partially dried (H,Pb,Fe)TEAN, (H,Pb)TEAN/sWheat, and (H,Pb,Fe)TEAN.

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, Içbudak, Yilmaz, and Olmez [42] 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 $La_5O_7NO_3$. 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 [43]. 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

HTEAN dried at 40°C for 2 h in Ar begins to decompose exothermically starting near 220°C, as shown in Figure 8. The decomposition is violently exothermic as illustrated by the rapid mass increase caused by the rapid production of gases, which forces the TG to register a very rapid mass increase and is accompanied by ejection of sample.

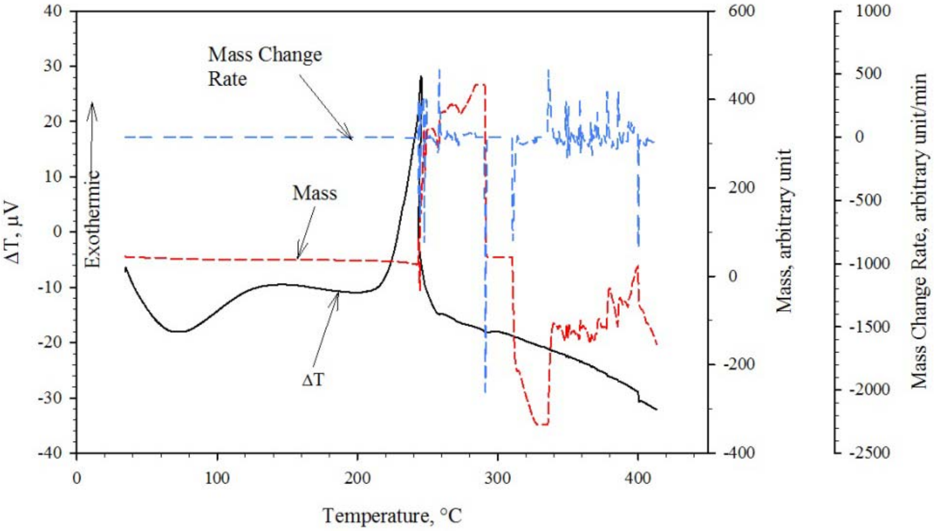

Figure 8. Thermal behavior of HTEAN as measured by TG/DTA at 5°C/min in Ar. Dried at 35°C for 2 h in Ar.

When 0.3 M Pb was added to the 3.5 M HNO_3, the TG/DTA observed similar high temperature violent reactivity, which was accompanied by additional exothermic mass loss reactions shortly after beginning the analysis of partially dried (H,Pb)TEAN at 25°C. The DTA observed a series of exothermic reactions beginning near 30°C that culminated in a rapid exothermic mass loss and ejection starting at 40°C.

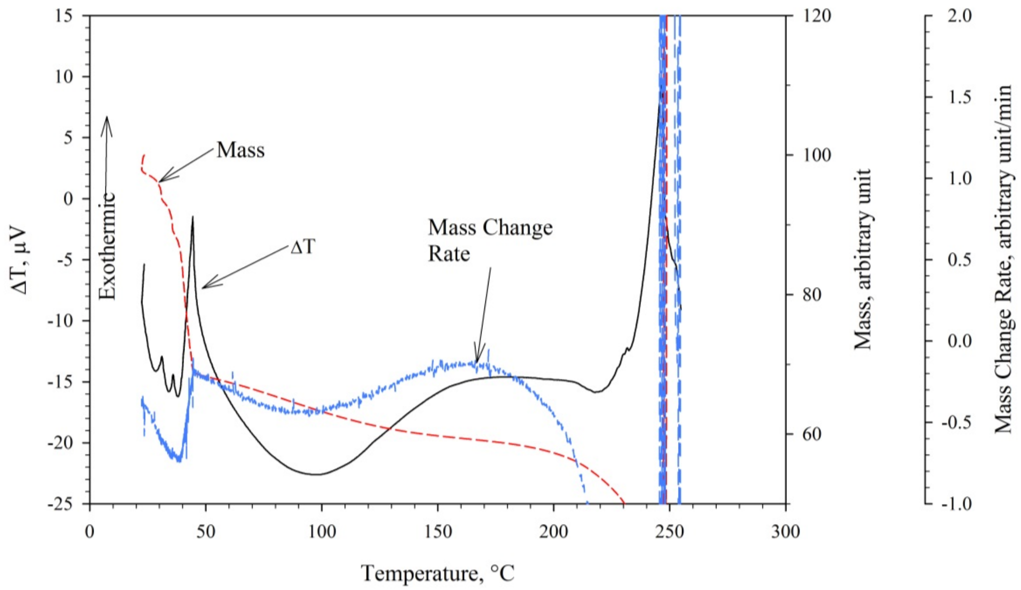

Figure 9. Thermal behavior of (H,Pb)TEAN as measured by TG/DTA at 5°C/min in Ar including drying at 45°C in Ar for 50 min.

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 over the weekend 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.

Figure 10 provides the results of the ARC analysis of 3.4 g of dried (H,Pb,Fe)TEAN. The figure shows that below 100°C, the ARC-observed several unsustainable exotherms with self-heating rates exceeding 0.01°C/min after each 10°C step increase; however, immediately after identification of exothermic behavior, the self-heating rate fell negative, resulting in only pressure and pressure change rate being presented. The absence of observed sustainable low-temperature reactivity could be a result of the drying approach. At 130°C, a self-sustaining exothermic reaction began and continued to 215°C, where 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°C/min, 210 bar, and 6000 bar/min, respectively, which indicate a very energetic and fast gas-producing reaction.

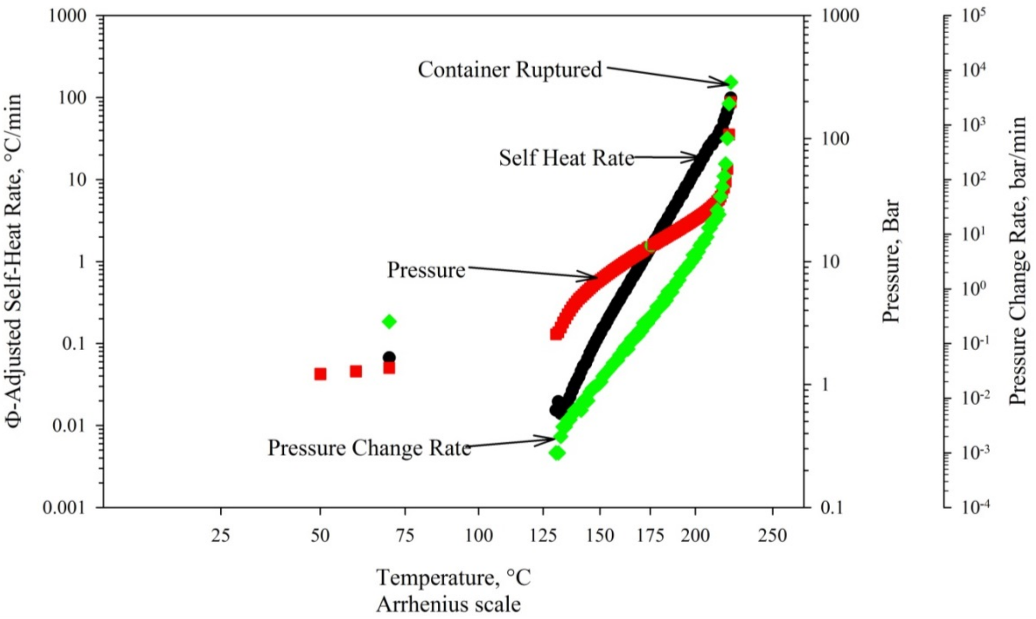

Figure 10. ARC-measured exothermic behavior of 3.4 g semi-dried (H,Pb,Fe)TEAN prepared in two stages, with the first addition dried for 3 days at 40°C and the combined second and first dried over the weekend at room temperature and 2 h at 40°C to 50°C in an Ar-dry box.

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

After neutralization, the liquid waste was solidified with sWheat. As shown in Figure 11, the TG/DTA of HTEAN/sWheat dried at 40°C in Ar found exothermic mass loss between 95 and 180°C, followed immediately by a second, more significant exothermic mass loss. When heated in air at 5°C/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.

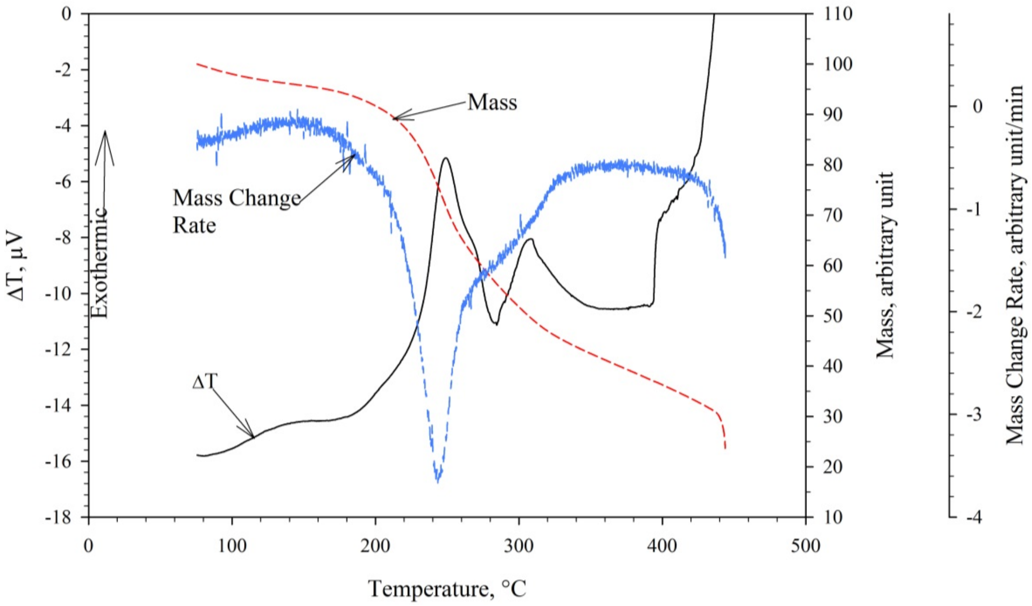

Figure 11. Thermal behavior of HTEAN/sWheat in Ar as measured by TG/DTA at 5°C/min. Sample dried at 40°C in Ar for 2 h.

Figure 12 shows that the ARC observed no exothermic behavior in undried HTEAN/sWheat until the sample was heated to 145°C, after which the mixture supports a self-sustaining reaction. It is likely that the evaporation of water prevents the observation of HTEAN's exothermic reactions below 100°C and the added thermal mass of sWheat delays the onset of the 125°C HTEAN decomposition observed for (H,Pb,Fe)TEAN.

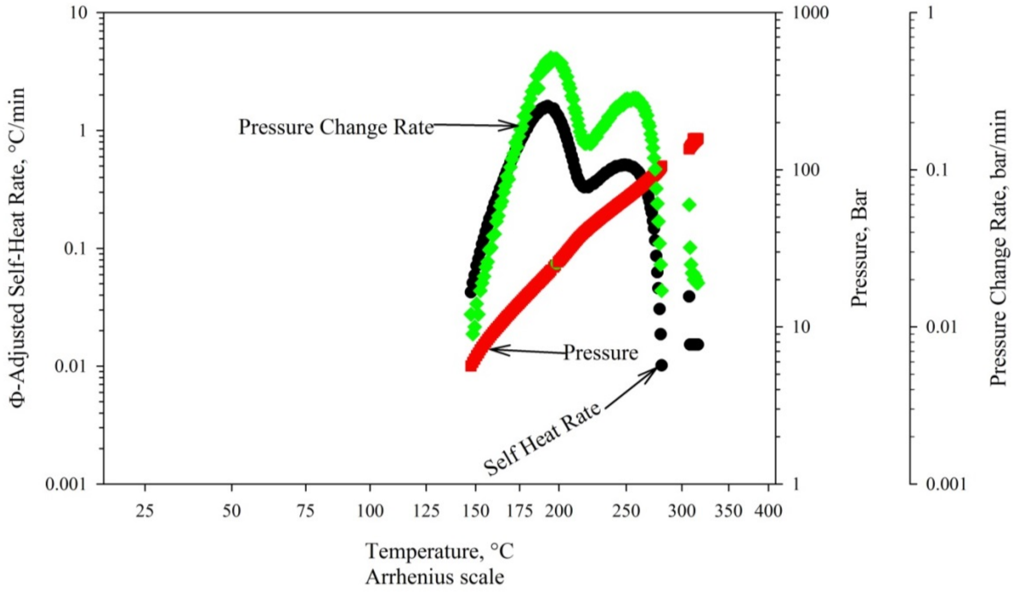

Figure 12. ARC-measured exothermic behavior of 2.8 g undried HTEAN/sWheat.

In contrast to undried HTEAN/sWheat, the ARC detected unsustainable exothermic reaction for the same amount of (H,Pb)TEAN/sWheat near 35°C (see Figure 13). This suggests that the addition of Pb heightens the thermal sensitivity of TEAN/sWheat. The onset of the significant self-sustaining reaction begins near the same temperature of 145°C.

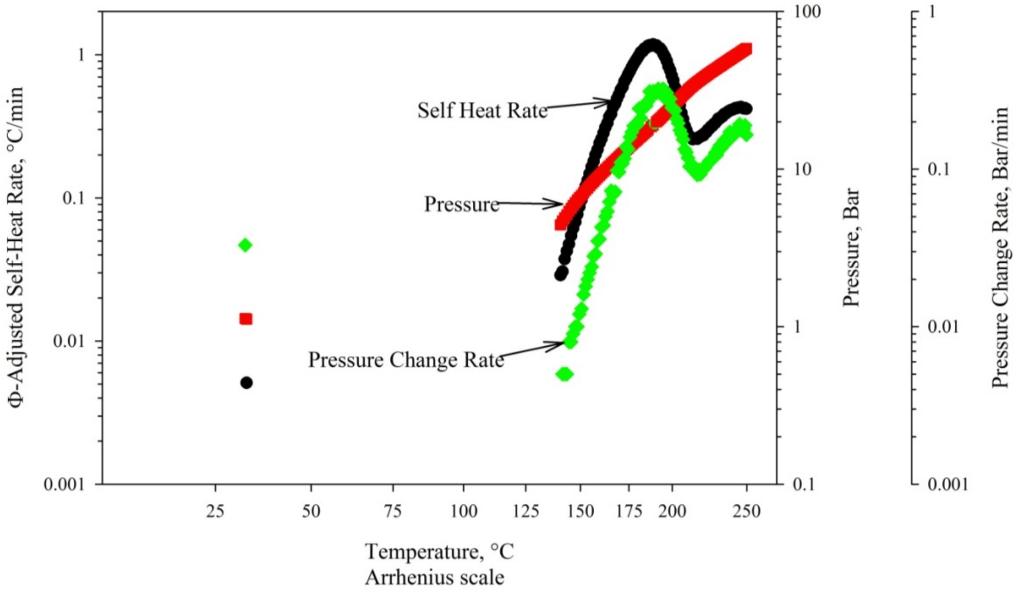

Figure 13. ARC-measured exothermic behavior of 2.8 g undried (H,Pb)TEAN/sWheat.

Comparison of Figure 8 and Figure 9 with Figure 14 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 are due to TEAN decomposition.

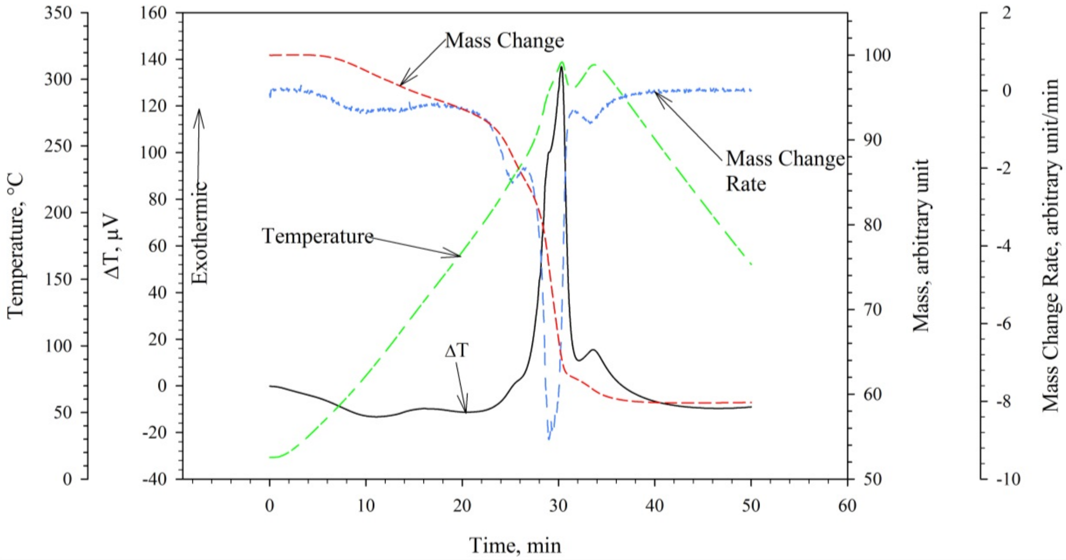

Figure 14. TG/DTA-measured thermal behavior of partially dried (H,Pb,Fe)TEAN/sWheat in air at 10°C/min as function of time. Sample dried for 11 d at room temperature in air.

For a partially dried (H,Pb,Fe)TEAN mixture dried at 50°C for 5.5 h, the ARC observed several unsustainable low-temperature exotherms below 125°C (see Figure 15), followed by a self-sustaining reaction beginning at 125°C, which led to a thermal runaway reaction 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 this TEAN, if not others, when dry will support low-temperature self-sustaining reactions similar to the HNO_3/sWheat. Additional testing of dried (H,M)TEANs and sWheat is needed to determine if these waste constituents can sustain self-sustaining reactions that are initiated near room temperature.

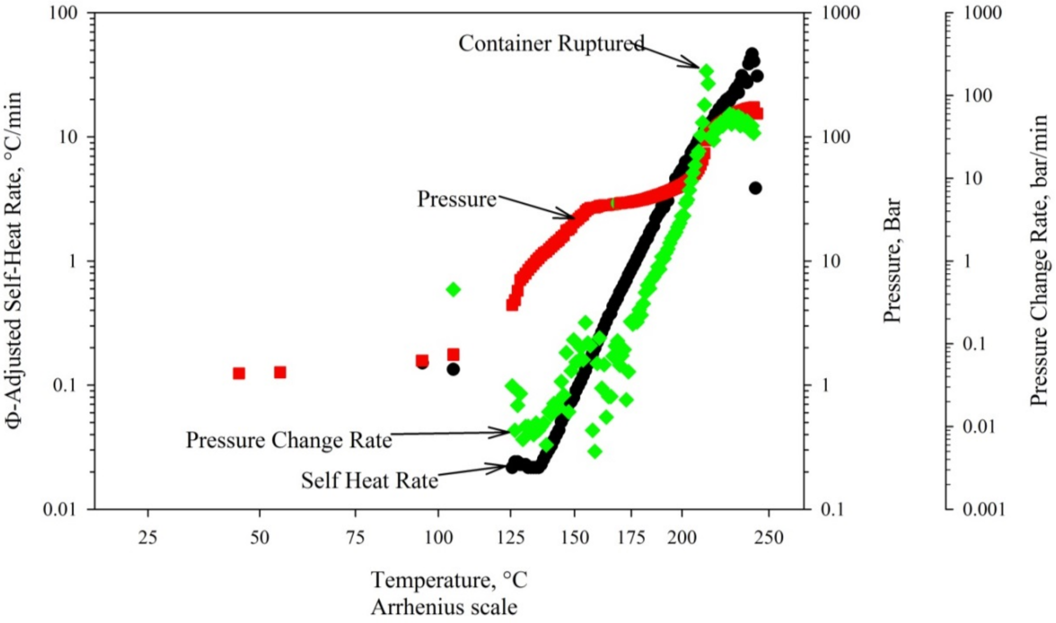

Figure 15. ARC-measured exothermic behavior of 9 g of (H,Pb,Fe)TEAN/sWheat dried at 50°C for 5.5 h in sample container.

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 reactive at temperatures as low as room temperature. The room temperature-reactive dried mixtures self-heated under adiabatic conditions to ignition at 80°C. Upon ignition, sample sizes of a few grams of a solid mixture produced gases sufficient to exceed pressures of 200 bar and rupture a robust titanium spherical reaction vessel. 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 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 adiabatic conditions to an 80°C energetic, rapid gas-producing thermal runaway reaction.
- Addition of lead nitrate to 3.5 M HNO_3 added an earlier initial onset reaction of nitrate with sWheat.
- (H,M)TEANs begin to decompose (self-react), producing heat and gases, beginning between 125°C and 150°C, eventually decomposing violently over 200°C.
- Mixtures of (H,M)TEANs and sWheat have similar decomposition onsets but do not decompose violently.
- 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 less than 100°C.

Because of the limited scope and duration of our probative tests, these findings do not represent a complete assessment of the susceptibility of all possible dried mixtures of 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. Testing using TG/DTA coupled with evolved gas analysis, ARC, and even larger-scale testing "cook-off" experiments is also recommended to evaluate aging of remediated waste constituents.

These studies illustrate the reactivity hazard of mixing a strong oxidant with fuel(s) and emphasize the importance of ensuring that TRU wastes containing oxidants and fuels are stable at all expected environmental conditions during generation, interim storage, transport, and over time following disposal. To avoid potential reactivity hazards at Department of Energy licensed nuclear disposal facilities, wheat-based pet litter should not be used to solidify and stabilize acidic nitrates, nor should TEA-neutralized nitric acid solutions of nitrate salts be allowed to dry completely.

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