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Probative Investigation of the Thermal Stability of Wastes Involved in February 2014 WIPP Waste Drum Breach Event

March 2015

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

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Summary

On February 14, 2014, a transuranic (TRU) waste drum breached in Room 7, Panel 7 of the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico. The breach released radioactive material internal and external to WIPP. The U.S. Department of Energy (DOE) reported that the breach occurred 72 days after Los Alamos National Laboratory (LANL) generated the TRU-waste drum and 16 days after the drum was emplaced in WIPP.[1]

In response, DOE commissioned a Technical Assessment Team (TAT) to determine, to the extent feasible, the particular mechanism(s) and chemical reactions that resulted in the failure of the waste drum and release of material in WIPP.[1] The TAT assembled a diverse group of national laboratory scientists to conduct technical evaluations that included Pacific Northwest National Laboratory (PNNL), who was tasked with 1) chemically and physically characterizing samples obtained from the lip of the breached drum and nearby locations and 2) performing limited phenomenological studies on the thermal behavior of the waste materials to define conditions that could have led to the event.

In support of TAT efforts, PNNL performed a probative set of thermoanalytical experiments to determine the thermal reaction sensitivities of representative mixtures of waste constituents and the absorbent and the neutralization agent used in LANL's waste remediation process. PNNL, with TAT input, selected a limited set of simulated remediation products and simulated 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 Drum 68660. Previous studies at PNNL and by others that determined the thermal stabilities of cellulose and different nitrate salts and amine-based complexants helped focus the small test matrix to mixtures of the absorbent Swheat Scoop® (Swheat) and nitric acid, the triethanolamine (TEA) nitrate salts produced from neutralization of nitric acid and nitric acid solutions containing selected nitrate salts with KolorSafe® (Kolorsafe), and these TEA-neutralized nitrate salts mixed with Swheat.

PNNL used simultaneous thermogravimetric and differential thermal analysis (TG/DTA) and accelerating rate calorimetry (ARC) experiments to determine the thermal sensitivities of components and mixtures of components characteristic of waste materials expected in Drum 68660. Overall, the probative thermoanalytical studies using TG/DTA and ARC show that the TRU-waste remediation process used to generate the wastes in Drum 68660 produced thermally reactive individual constituents and mixtures that can react vigorously and energetically produce gases. Some of the compounds and their mixtures are susceptible to low-temperature (less than 100°C) reactions that can self-heat under adiabatic conditions to thermal runaway conditions, while others had ARC-observed exotherms below 100°C that could not sustain a heating rate sufficient to heat the sample, likely because they were overcome by evaporation of water. Other materials are susceptible to self-heating reactions starting at 125°C or greater that lead to thermal runaway reactions.

[1] U.S. Department of Energy. 2014. *Waste Isolation Pilot Plant Recovery Plan*, Rev. 0, Washington, D.C. http://www.wipp.energy.gov/Special/WIPP%20Recovery%20Plan.pdf.

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Following is a summary of the thermoanalytical study results:

- During adiabatic ARC tests, two mixtures of 3.5 M nitric acid and Swheat, one dried overnight and the other for 8 days, began to self-heat immediately upon initiation of the experiment at 30°C and 40°C, respectively, and both led to a rapid, energetic thermal runaway reaction at 80°C with sufficient gas and heat production to rupture the spherical sample container; the sample container is rated to withstand a pressure of over 300 bar (300 kPa). The samples were passively dried at room temperature (15°C to 18°C) in air. This mixture was used to simulate a portion of the acidic nitrate salt waste fraction within Drum 68660.
- TG/DTA testing indicated that addition of lead nitrate to 3.5 M HNO_3 reduces the onset temperature of the initial exothermic reaction with Swheat from 110°C to 100°C.
- The mixture of Kolorsafe (aqueous triethanolamine) and nitric acid, used to simulate a major constituent in the liquid waste fraction in Drum 68660, will produce hydrogen triethanolamine nitrate (HTEAN) that thermally decomposes in ARC tests starting between 125°C and 150°C. This self-heating under adiabatic conditions eventually initiates a vigorous and energetic gas-producing thermal runaway reaction near 210°C.
- Mixing HTEAN and/or hydrogen and metal ion TEAN [(H,M)TEAN] with Swheat slows the HTEAN or (H,M)TEAN decomposition rate.
- ARC testing involving HTEAN, (H,M)TEAN, HTEAN/Swheat, and (H,M)TEAN/Swheat mixtures, which were used to simulate the liquid waste fraction in Drum 68660, identified exothermic reactions occurring at temperatures below 100°C and observed self-sustaining reactions starting at 125°C to 150°C that eventually led to thermal runaway.
- Systems containing significant water content could not sustain self-heating reactions below 100°C.
- TG/DTA testing of dried hydrogen, lead, and iron TEAN [(H,Pb,Fe)TEAN]/Swheat in air found exothermic reactions at temperatures less than 100°C.
- TG/DTA testing showed that over-neutralization alters the thermal exothermic reaction profile and slows the TEAN/Swheat exothermic reaction.
- TG/DTA testing indicated that under-neutralization of nitric acid by Kolorsafe alters the thermal exothermic reaction profile and accelerates the TEAN/Swheat exothermic reaction.

The Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers has published guidance for using TG/DTA- and ARC-measured reaction onset temperatures to establish safe process operating temperatures. The CCPS indicates that processes should be safely managed if the process temperature is kept at least 100°C below a TG/DTA-measured onset temperature and at least 50°C below an ARC-measured onset temperature; operating at temperatures within those boundary temperatures requires engineering controls.

Because of the limited scope of these probative studies, these studies are incomplete and could not definitively identify the waste fraction or constituent in Drum 68660 that has low-temperature reaction susceptibilities that may have led to the TRU-waste drum breach at WIPP. These studies did show that combinations of waste constituents and remediation materials can form thermally sensitive compounds and/or mixtures that can self-heat under certain physical conditions to temperatures where thermal runaway reactions producing heat and gases can occur. This report provides results of PNNL's studies investigating the thermal sensitivities and behavior of suspect simulated remediated wastes.

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Acronyms and Abbreviations

(H,M)TEAN	hydrogen and metal ion triethanolamine nitrate
(H,Pb)TEAN	hydrogen and lead triethanolamine nitrate
(H,Pb,Fe)TEAN	hydrogen, lead, and iron triethanolamine nitrate
ARC	accelerating rate calorimetry
ASO	Analytical Support Operations
CCPS	Center for Chemical Process Safety
DOE	U.S. Department of Energy
DTA	differential thermal analysis
EDTA	ethylenediaminetetracetate
HEDTA	hydroxyethylethylenediaminetriacetate
HTEAN	hydrogen triethanolamine nitrate
Kolorsafe	KolorSafe®
LANL	Los Alamos National Laboratory
mp	melting point
PFP	Plutonium Finishing Plant
PNNL	Pacific Northwest National Laboratory
PVC	polyvinyl chloride
QA	quality assurance
RH	relative humidity
Swheat	Swheat Scoop®
TAT	Technical Assessment Team
TEA	triethanolamine
TEAN	triethanolamine nitrate
TG/DTA	thermogravimetric and differential thermal analysis
TGA	thermogravimetric analysis
TI	test instruction
TRU	transuranic
WIPP	Waste Isolation Pilot Plant

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1.0 Introduction

On February 14, 2014, a transuranic (TRU) waste drum, 68660 (Wallace et al. 2014; Clark and Funk 2014), breached in Room 7, Panel 7 of the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico. The breach released radioactive material internal and external to WIPP. The U.S. Department of Energy (DOE) reported that the breach occurred 72 days after Los Alamos National Laboratory (LANL) generated the TRU-waste drum and 16 days after the drum was emplaced in WIPP (U.S. Department of Energy 2014).

In response, DOE commissioned a Technical Assessment Team (TAT) to determine, to the extent feasible, the particular mechanism(s) and chemical reactions that caused the waste drum to be breached and release material in WIPP (U.S. Department of Energy 2014). The TAT assembled a diverse group of national laboratory scientists to conduct technical evaluations that included 1) chemical and physical characterizations of samples obtained from the lip of the breached drum and nearby locations and 2) limited phenomenological studies on the thermal behavior of the waste materials that could have led to the event (Wilson et al. 2015).

In support of the TAT's efforts, Pacific Northwest National Laboratory (PNNL) performed a probative set of thermoanalytical experiments to determine the thermal reaction sensitivities of representative mixtures of waste constituents and the absorbent and neutralization agent used in LANL's waste remediation process. PNNL, with TAT input, selected a limited set of simulated remediation products and simulated 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 Drum 68660. Previous studies at PNNL and by others that determined the thermal stabilities of cellulose and different nitrate salts and amine-based complexants helped focus the small test matrix to mixtures of nitric acid and a wheat-based organic kitty litter known as unscented Swheat Scoop® (Swheat)—which was used as an absorbent in remediation/ repackaging activities beginning in October 2012 (Wallace et al. 2014), the triethanolamine (TEA) nitrate salts produced from neutralization of nitric acid and nitric acid solutions containing selected nitrate salts with KolorSafe® (Kolorsafe) beginning after September 2013 (Wallace et al. 2014), and these TEA-neutralized nitrate salts mixed with Swheat. This report provides the results of these experimental studies.

2.0 Drum 68660 Waste and History

The breached drum contained remediated wastes resulting from plutonium recovery and purification operations, including nitrate-bearing waste streams evaporated to near dryness, the non-oxalate wastes washed with 3.3 M HNO_3, and various refuse from processing including glovebox debris. This waste was placed into lead-lined drums and stored for roughly 30 years before being segregated, processed, and treated for disposal to WIPP.

The TRU-waste in the breached drum was from the LA-MIN02-V.001 (MIN02) waste stream (Chancellor 2014). According to Chancellor and a working draft by Clark and Funk (2014), the remediated MIN02 wastes contained various metal cations, the oxidizing agent nitrate anion, and Swheat. Prior to October 2012, other organics—such as aged oxalate wastes and Kolorsafe, an organic based

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commercial neutralizing agent containing triethanolamine as its active ingredient—were also present in the waste or added to it during remediation.

2.1 Acidic Metal Nitrate Salt Waste

The nitrate salt waste that was repackaged into Drum 68660 was taken from the parent Drum S855793, which was generated in October 1985 and contained 14 bags of nitrate salts, 4 of which resulted from an oxalate precipitation process (Wallace et al. 2014). Based on historical records, the metal ions present as nitrates included Ca, Mg, K, Fe, Na, Al, Cr, Ni, and Pb (Clark and Funk 2014).

Drake's (2014) analysis of the nitrate salt samples taken from two unremediated drums, produced in 1980 and 1981, respectively, indicated the following elements were present: Ca, Mg, K, Fe, Na, Al, Cr, Ni, Pb, Zn, and U. Although the samples had similar nitrate content, the metal concentrations varied considerably. For example, the Na and Ca concentrations varied by factors of 2.8 and 300, respectively. The variation in elemental composition is not unexpected given the variety of materials processed in the plutonium processing facilities at LANL. The metal nitrate salts in Drum 68660 would be expected to be largely composed of the alkali (Na, K) and alkaline earth (Mg, Ca) elements, with lower amounts of other transition metals (Fe, Cr, Ni, Zn), main group (Al, Pb), and actinide (U, Pu, Am) elements (Clark and Funk 2014; Schwantes et al. 2014). The TAT and LANL personnel were unable to find a more detailed description of the chemical composition of the nitrate salt waste contained in Drum 68660.

Oxalate was used in the plutonium processing operations and would have been a component in residues sent for evaporation and formation of salts. Oxalate is decomposed to CO_2 in 0.1 to 6 M nitric acid and in the presence of metal catalysts such as manganese and vanadium (Nash 2012). Typically, the solutions are heated to about 100°C to increase the rate of decomposition. After storage of the parent drum containing nitrate salts for just over 28 years at ambient conditions, the concentration of oxalate in the nitrate salts is not known. However, given the acidity and length of time, the oxalate concentration would be expected to be much lower than when the salts were first generated (Wallace et al. 2014).

2.2 Remediation Process, Chemicals, and Materials

To remediate the waste, first the liquids were decanted and neutralized with Kolorsafe to pH 7 based on pH paper measurement (Clark and Funk 2014; Wallace et al. 2014). Kolorsafe is a pH 10.2 aqueous solution containing 52.954 wt% TEA (3.87 M TEA) and a pH indicator Alizarin (NPS Corporation 2014a; NPS Corporation 2014b). Neutralization of the acidic waste solutions would result in a solution or slurry of hydrogen triethanolamine nitrate (HTEAN), and a combination of hydrogen and metal triethanolamine nitrate [(H,M)TEAN] is assumed.

TEA is a Lewis base or electron pair donor and will bond with electron pair acceptors such as hydrogen ion or other cations (Fowkes and Harrison 2006; Yilmaz et al. 2002; Whitmire et al. 1999; İçbudak et al. 1996; Içbudak et al. 1995; Neilsen et al. 1972; Brannon et al. 1971; Sen and Dotson 1970; Naiini et al. 1995). According to the Dow Chemical Company, the mono-, di-, and tri-ethanolamines are mildly alkaline and will react with acids to form salts or soaps, and as alcohols they are hygroscopic and can be esterified (Dow Chemical Company 2014).

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The Swheat used to absorb the liquid in the liquid and salt fraction of the waste in Drum 68660 is derived from the whole grain of wheat (Sladek 1997; Pet Care Systems 2015). Shewry et al. (2013) and Sramkova, Gregova, and Sturdik (2009) report that wheat kernels are composed of three parts:

1. 13% to 15% bran or outer shell,
2. the endosperm, which comprises nominally 80% to 85% of the kernel's mass, and
3. the germ, which comprises 2 to 3 mass%.

The endosperm is nominally 83% starch, 13% proteins and enzymes, 1.5% fats, 1.5% dietary fibers, and 0.5% minerals. The bran is a complex mix of cellulose, lignin, pentosans, and polymers based on xylose and arabinose, which are tightly bound to proteins. Starch and proteins are the predominant kernel constituent at 65% to 70% and 14%, respectively.

To solidify the neutralized liquid waste, a volume (vol) ratio of 3:1 Swheat to neutralized liquid waste was used. The unneutralized wet, acidic salt wastes were mixed with Swheat to absorb any remaining liquid. The prescribed level for Swheat addition was 3 volume parts Swheat to 1 volume nitrate salt (Clark and Funk 2014). The TAT estimates that the Swheat-to-nitrate-salt volume ratio was much lower, at roughly 0.7:1.

2.3 Drum 68660 Contents

When Drum 68660 was originally loaded, the glovebox refuse was first placed on the bottom of drum, followed by the neutralized and absorbed liquid wastes, and finally absorbed salt wastes. After the drum was filled to about 60% of capacity, the PVC liner bag was likely "horse-tailed" and taped closed, the drum lid installed, and the drum removed from the glovebox. The combination of the oxidizing nitrate salt residues, the 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 (CCPS 1995).

Water's thermochemical properties and physical behavior below 100°C, and its presence as a major constituent in the Drum 68660 waste, mean that it could have played a major role in preventing a thermal runaway reaction in the remediated waste. Prior experience managing TRU wastes generated at Hanford's Plutonium Finishing Plant (PFP) suggests that any contained water and some of the nitric acid in the Drum 68660 waste likely would evaporate over time. In PFP operations, TRU-waste would first be packaged in horse-tailed robust PVC plastic bags, then packaged in two to three vented plastic bags and placed into a TRU drum with a WIPP-approved NucFil® filter. TRU waste drums generated at the PFP were sent to the Hanford Waste Receiving and Processing Facility for inspection prior to being sent to the WIPP. In 2003 and 2004, several TRU drums were returned from the Waste Receiving and Processing Facility for repackaging. When PFP staff opened the returned waste drums, the contents were noticeably drier than when the drums had been packed months earlier.

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3.0 Reported and Possible Reactivities

The principal waste components within Drum 68660 that are susceptible to chemical reactions include hydrogen or metallic TEANs [(H,M)TEAN], Swheat, incompatible mixtures of (H,M)TEAN and Swheat [(H,M)TEAN/Swheat], HNO_3 and Swheat (HNO_3/Swheat), and TEA and nitrate salts (TEA/NO_3^-). The TEANs can energetically thermally decompose because of the intramolecular oxidation/reduction potential of the nitrate and the organic ethanol groups (e.g. nitrate to C-C bond). Swheat is combustible in air (Jenkins et al. 1998). In addition to the thermal instability of TEAN, TEAN and Swheat mixtures are potentially reactive because of the close association of nitrate and a fuel glucose-polymer. HNO_3/Swheat and (H,M)TEAN/TEA/Swheat represent incompatible mixtures of an oxidizing agent nitrate with an organic fuel. This section provides available results reported in the literature on reactions of organic materials with nitrates and/or nitrites.

3.1 TEA, HTEAN, and Other TEA Complexes and Salts

As a potential major constituent in the neutralized waste fraction, TEA [$N(CH_2CH_2OH)_3$] could be a major fuel source and reactant or major contributor to the overall system's chemistry. TEA is a viscous organic compound that features a tertiary amine and three primary alcohol groups. TEA melts at 21.6°C and exhibits high thermal stability as evidenced by its boiling point of 335.4°C (Speight 2005).

TEA is a polyfunctional ligand that is capable of bonding through its nitrogen and/or oxygen atoms and forms complexes with metal ions (Fowkes and Harrison 2006). Since TEA is a Lewis base due to its free pair of electrons on the nitrogen, it can protonate at the nitrogen and bond with metal ions such as Ni(II) (Neilsen, Hazell and Rasmussen 1972) or La (Fowkes and Harrison 2006), which are both Lewis acids and form nitrate salts. The Cambridge Structural Database includes complexes of TEA with multiple metal ions including Li, Zn, Cu, Ba, Ni, Mn, Hg, Pb, Cd, Y, Pr, and Y (Allen 2002). Dow Chemical markets ethanolamines based on their combined amine and alcohol moieties. According to DOW, as amines, ethanolamines are mildly alkaline and can react with acids to form salts or soaps. As alcohols, they are hygroscopic and can be esterified (Dow Chemical Company 2014). The use of TEA adds another dimension of chemical complexity and potential reactivity to the waste contained within Drum 68660.

Reaction of TEA with HNO_3 produces HTEAN. 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 (Cronin and Brill 1988). Gases released included CO_2, N_2O, CO, NO, NH_3, and HCN. This mixture of nitrogen oxide oxidants and the fuels CO, NH_3, and HCN is also potentially reactive, particularly if confined. In addition, the gaseous nitrogen oxides can react with the fuel constituents in the waste mixture, particularly if confined. Thus, protonation of TEA to produce the protonated nitrate salt results in a more thermally unstable chemical compound whose decomposition products can participate in secondary exothermic reactions.

Metal complexes of TEA exhibit variable thermal stabilities. Using DTA and TGA at a heating rate of 10°C/min, Içbudak, Yilmaz, and Olmez (1996) found that the decomposition in nitrogen of the TEA nitrate salts of La, Ce(III), and Nd(II) was "violently exothermic." 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.

Yilmaz, Topcu, and Karadag found that TEA and saccarharinate ($C_7H_5NO_3S$) (sac) forms complexes with divalent Mn, Fe, Co, Zn, Cd, and Hg having the general form $[M(TEA)_2](sac)_2$, where M represents the divalent metal ion. Their spectral and structural studies found that the TEA behaves as a N, O, O'-donor tridentate ligand in with all these metal ions while the sac acts as a counter-ion (Yilmaz, Topcu and Karadag 2002).

Yilmaz and his coworkers (Yilmaz, Topcu and Karadag 2002) used simultaneous thermogravimetric and differential thermal analysis (TG/DTA) at a heating rate of 10°C min^{-1} under a nitrogen (N_2) purge to determine the thermal stability of these saccarharinate complexes. Exothermic onset temperatures ranged from 114°C for Hg(II) to 223°C for Ni(II). They attributed this decomposition to the loss of two CH_2OH radicals produced from the TEA. The resulting moiety loses the remaining portion of the TEA and decomposes later to form $Mn(sac)_2$. The complex eventually thermally decomposes to the metal.

Içbudak, Yilmaz, and Olmez (1996) also investigated the thermal stabilities of the chloride TEA salts of Cr(III), Fe(III), Ru(III), and Rh(III) and found a mixture of endothermic and exothermic decompositions, depending on the metal. They describe the complex Cr(III) salt decomposition that began at 130°C as endothermic. The Fe(III) decomposes in both endothermic and exothermic events, with the first exotherm assigned to 190°C. They describe the Ru(III) salt decomposition beginning near 120°C as endothermic, although the material did exhibit some exothermicity. The Ru(III) chloride salt begins decomposing at 130°C followed by melting at 170°C, which leads into an endothermic decomposition. The Cr formed its oxide and the others were reduced to their metals. In air, the decompositions were similarly complex but were exothermic and formed the oxides in all cases.

In addition to the reported thermal reactivities, the formation of metal-TEA complexes could serve as a catalyst for the oxidation and nitration reactions, allowing the reactions to proceed at lower temperatures and faster rates.

3.2 Glucose-Based Materials Reactions with Nitrate and Nitrite Salts

Beitel found in his combustibility studies that simulated Hanford salt cake/sugar mixtures reacted violently at 25% sugar, but at 10% sugar no combustion occurred (Beitel 1976). In studies to evaluate the effectiveness of sucrose as a denitrating agent for Hanford wastes, Scheele and coworkers (Kim et al. 2005) using TG/DTA found that sucrose began to react exothermically with nitrate and nitrite in a simulated alkaline Hanford waste principally composed of nitrate and nitrite salts, but with percent or slightly lower levels of a variety of constituents. The gases N_2O, CO_2, and CO were observed in sealed container tests, indicating oxidation; the formation of the reactive oxidants NO and NO_2 cannot be discounted because of the possibility that the tests being performed in sealed containers permitted back reaction with sucrose.

In studies supporting PFP Pu glovebox decontamination operations, Scheele and coworkers (Scheele et al. 2005) used TG/DTA and accelerating rate calorimetry (ARC) to study the thermal reaction sensitivities of cotton and cotton/nylon cloths (cellulose-rich cloths, i.e., polysaccharide-rich cloths) saturated with nitric-acid-based decontamination agents and neutralized with sodium hydroxide or sodium carbonate. In cloths containing dried sodium hydroxide neutralized solutions of 1 M HNO_3 and ceric and

cerous nitrates, the ARC observed reaction onsets at temperatures as low as room temperature. The age of the dried cloths affected thermal sensitivity with the ability of the cloth to sustain self-sustaining reactions increasing at lower temperatures up to 114 days and decreasing for a 149-day-old cloth. For 100% cotton cloths containing a sodium hydroxide-neutralized solution of HCl, NH_4F, citric acid, nitric acid, and proprietary buffering agents, the ARC observed a self-sustaining reaction beginning at 120°C, while the unneutralized cloths began to react at 70°C, indicating increased susceptibility at acidic conditions.

In studies investigating the use of cellulose to denitrate a Hanford waste, Scheele and coworkers (Scheele et al. 2008; Scheele et al. 2007), using 10 to 50 mg-scale TG/DTA and 1 to 6 g ARC studies (Scheele, McNamara and Bagaasen 2008; Scheele et al. 2007), found that a simulated waste mixed with cellulose begins to react at a lower temperature than a neat mixture of sodium nitrate and cellulose, suggesting catalytic behavior by other waste constituents. Mixtures of cellulose and sodium nitrate with cellulose-to-nitrate ratios ranging from 75% to 1300% of stoichiometric cellulose had reaction onset temperatures ranging from 190°C to 220°C depending on sample mass. In the ARC experiment using 2.5 g, the ARC observed self-heating rates of greater than 1000°C min^{-1}. In another experiment, a 1-g sample of cellulose-containing simulated waste (C:N = 0.75) began a self-sustaining reaction at 115°C. The mass spectroscopy-measured residual gases from cellulose-containing simulated waste include N_2O, NO, H_2O, and CO_2; it is likely that most of the NO_x produced reacted with organics in the simulated waste since the experiments were performed in sealed containers. These experiments indicate that the oxidation reactions between cellulose and nitrate and/or nitrite can begin at lower temperatures when other compounds such as metal nitrates are present.

Once known, reaction rate parameters can be used to predict and model the behavior and heat production rate for a chemical system, and thus could, for example, be used to model the thermal behavior of a TRU-waste drum. Of particular interest for Drum 68660 is the reaction between Swheat and the nitrate salts. For the onset reaction at 290°C between sodium nitrate and cellulose (a major constituent in Swheat), the activation energy (E_a) and Arrhenius preexponential (A) were 186 kJ $mole^{-1}$ and 3×10^{14} s^{-1}, respectively (Scheele et al. 2007). E_a for many common reactions is 50 kJ $mole^{-1}$, which will have a doubling of the reaction for every 10°C increase in temperature (Adamson 1979). For the onset reaction at 290°C between sodium nitrate and cellulose, a 10°C increase will increase the rate by a factor of 14. This reaction could be of concern should other reactions raise the temperature to this level.

3.3 Reactions of Amino- and Carboxylate-Organic Complexants with Nitrates and Nitrites

Studies by Scheele and coworkers to determine the reactivity of nitrate- and organic-rich Hanford wastes (Scheele et al. 1995) resulting from used or amino and carboxylate complexants provide additional insights into the effects of other waste constituents. These studies investigated the thermal stability of 2, 6, and 10 mass% total organic carbon admixtures of nitrate and/or nitrite with the sodium salts of acetate, citrate, ethylenediaminetetracetate (EDTA), and hydroxyethylethylenediaminetriacetate (HEDTA), and a simulated organic complexant-containing Hanford waste.

The neat mixtures began reacting between 180°C and 290°C as measured by the ARC, which is often below the melting point (mp) of the nitrate and/or nitrite salt. A 0.7-g sample of simulated organic-and nitrate-rich Hanford waste containing a variety of metal salts and complexants began a self-sustaining

reaction near 120°C, much lower than would have been predicted based on the admixtures of the pure reactants. This reduction in onset temperature suggests that the constituents in the waste had a synergistic effect that possibly could include catalysis by the metal ion constituents. The gaseous products from these reactions included CO_2, N_2O, H_2O, and NH_3, depending on the organic.

4.0 Experimental Considerations

This section provides 1) the basis for the experimental approach, 2) the instruments and methods used for the thermoanalytical tests, and 3) a description of the testing materials, their preparation, and some chemical and physical characteristics. Excel Version 14.0.7143.5000 was used for preliminary evaluations and calculations and preparation of data for graphical presentation in this report using SigmaPlot for Windows Version 12.5 Build 12.5.0.38.

4.1 Experimental Strategy

This section provides the basis for the experimental strategy used in the limited study to determine whether suspect individual waste constituents or representative combinations were susceptible to thermally initiated chemical reactions that could have resulted in a thermal runaway and breach of Drum 68660.

Drum 68660 contained two major TRU-waste components: acidic liquids and acidic salts. Based on a review of LANL reports and records, the TAT decided to use a conservative acidity value of 3.5 M HNO_3 as the nominal acidity for simulating Drum 68660 wastes during experiments. The acidic liquid fraction was neutralized with Kolorsafe (TEA) and then mixed with 3 volumes of Swheat to absorb free liquid. The salt fraction was mixed with Swheat to absorb the remaining free, interstitial, and occluded acids. The salt waste fraction would be a mixture of nitrate salts and HNO_3 absorbed into Swheat.

The potentially reactive constituents and mixtures are therefore (H,M)TEANs, Swheat, (H,M)TEANs and Swheat mixtures [(H,M)TEAN/Swheat], HNO_3 absorbed into Swheat (HNO_3/Swheat), nitric acid solution of metal nitrates [(H,M)NO_3] absorbed into Swheat [(H,M)NO_3/Swheat], and nitrate salts mixed with Swheat (salt/Swheat). The specific metal cation is substituted for M when known. For this limited scope study, each potentially reactive mixture type was tested with the exception of the salt/Swheat.

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 (CCPS 1995). For a waste chemical system to be safe, the engineered system must be able to dissipate any heat produced at a rate that will prevent temperatures from rising to the level where the chemical reaction rate(s) produce heat faster than the engineered system can dissipate the heat.

The CCPS identifies the important factors affecting chemical stability (CCPS 1995). These factors 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 causing the reaction rate to increase by a factor between roughly 2 and 4, in general. The nature of the reactants determines the susceptibility to reaction through its functional group(s), the reaction's possible potential energy, and its potential to produce gaseous products. The CCPS list of systems meriting consideration or designated as incompatible includes mixtures of organics and oxidizers other than oxygen, such as nitrates and nitrites. The reactants' concentrations control the reaction rate since the rate is roughly proportional to the reactants' concentrations. Impurities can have catalytic effects by reducing E_a, thus increasing the reaction rate and decreasing the reaction's onset temperature. 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.

Water or liquid content in the waste after more than 70 days of storage is an important unknown that could have affected the chemical stability of the waste. Representing the majority of the contents in Drum 68660, absorbed liquid in the Swheat would be expected to prevent a significant temperature increase by dissipating any heat generated internally by any exothermic chemical reactions. Water would be expected to confound or mask attempts to identify reactivity at near-room temperature. Water is particularly effective as a heat sink because of its significant heat capacity at constant pressure (C_p) of 4.179 J g^{-1} °C^{-1} (75.2 J mol^{-1} °C^{-1}) at 298.15°C and its significant heat of vaporization (ΔH_{vap}) of 2.27 kJ g^{-1} (40.893 kJ mol^{-1}) (Barin 1989). Water can absorb significant amounts of chemically produced heat below 100°C.

Taking into consideration the CCPS-identified critical reactivity factors, the nominal composition of the TRU wastes before remediation, the materials and process used to remediate the TRU waste, and the effects of storage, simultaneous TG/DTA and ARC were used to investigate the thermal susceptibility of selected individual remediated waste constituents. This was done both in aerobic and anaerobic conditions, combinations postulated to be representative of remediated liquid and salt waste fractions, the effects of two selected waste constituent metal ions, and the effects of liquid content.

4.2 Instruments

To determine the thermal sensitivities of the tested surrogate waste mixtures, a Seiko 5200 simultaneous TG/DTA and Thermal Hazards Technology ARC was used. TG/DTA measures mass changes and temperature differences between the sample and a reference material, which in this case was alumina. The TG/DTA was located in a fume hood on a marble slab to minimize disruptive vibrations.

In this use, the TG/DTA was used to determine the onset temperatures of reactions and to qualitatively determine whether an observed reaction gained or lost mass while producing heat (exothermic) or requiring heat (endothermic). The instrument was temperature calibrated using 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) melting point standards 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 for the duration of the experiments based on multiple confirmatory measurements. No mass calibration was performed. The results presented for the DTA are baseline-corrected by the instrument except for the two experiments using (H,Pb,Fe)TEAN/Swheat, which had good baselines without correction. The TG/DTA experiments used either static room air or an ultra-high purity Ar purge and a heating rate of 5°C/min, except for the two

tests of (H,Pb,Fe)TEAN/Swheat, which used a heating rate of 10°C/min. Testing was performed under the following test instructions (TIs):

- 66707-TI-020, Rev. 0, *WIPP Technical Assistance – Simultaneous Differential Thermal Analysis/ Thermogravimetric Analysis (DTA/TGA)*
- 66707-TI-020, Rev. 1, *WIPP Technical Assistance – Simultaneous Differential Thermal Analysis/ Thermogravimetric Analysis (DTA/TGA)*

The ARC provided a more sensitive measure of 1) an exothermic reaction's onset temperature than TG/DTA, 2) whether an exothermic reaction could heat the material to higher temperatures, and 3) whether that reaction could support heating the sample to a temperature where thermal runaway could occur. The ARC reports only exothermic behavior. The ARC operated as an adiabatic calorimeter in a heat/wait/search mode using samples sizes ranging from 2.5 to 8 g in a nominal 10-mL titanium sample container. In the heat/wait/search mode, the ARC begins at an operator-selected temperature, equilibrates for an operator-selected time at temperature, and then monitors the sample to determine if the sample is self-heating. When no self-heating is observed (heating rate > 0.01°C/min), the temperature is increased by an operator-selected amount and the heat/wait/search process is repeated until the ARC observes self-heating. When self-heating is detected, the ARC enters its adiabatic mode, maintaining the calorimeter temperature at the same temperature at which the sample self-heats, and periodically reports self-heat rate in °C/min, pressure in bar, and pressure change rate in bar/min. If the self-heat rate falls below the operator-selected exothermic criteria because the reaction stops or because of an endothermic event (e.g., melting or evaporation event), the instrument returns to its heat/wait/search mode and does not resume reporting until another exotherm is detected. To reflect the exothermic-only data, the results are presented as discrete measurements to avoid the misinterpretation that self-heating is occurring when non-exothermic events are occurring. The ARC is sealed so all product gases are retained in the container, which permits participation of the product gases in secondary reactions.

To prepare the ARC for use, the instrument is calibrated through a single run with an empty sample container and its temperature drift measured in one or more runs; typically a single drift run was performed. These two operations ensure excellent temperature stability throughout an analysis and for an extended time. The instrument was calibrated and its temperature drift measured each time a thermocouple was compromised as a result of a loss of sample containment. The ARC's original calibration and drift was used for the first five experiments, or for about 2 weeks. The instrument was again calibrated and the drift measured after a month for the next 2 months.

The ARC calibration run ensures that the calorimeter's jacket thermocouple and heater system respond properly to the sample thermocouple to ensure that an exotherm is detected. For the calibration run, the instrument heats stepwise by operator-selected temperature steps over an operator-selected temperature range and tunes the thermocouple/heater system. At each temperature step, the instrument holds at a temperature and adjusts the six proportional heaters located in the ARC's jacket until the calorimeter's four thermocouples match the sample thermocouple's temperature within the selected exothermic detection sensitivity, which for these experiments was from 0.001°C/min up to 0.01°C/min.

For the drift run that follows the calibration run, using the calibration file, the ARC operates in the normal heat/wait/search mode using an empty sample container. The magnitude and sensitivity of the temperature change rate or temperature drift is measured at all selected temperatures and must satisfy the operator-selected exotherm detection sensitivity.

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To accommodate the use of a metal container and its added thermal inertia in ARC testing, in a typical sample preparation, a titanium bomb would first be weighed and then a stainless steel nut and ferrule would be attached. Following this, the weight of the bomb would be measured again. The mass and heat capacity (C_p) of the titanium bomb and the mass and C_p of the sample would be used to calculate the added thermal inertia due to the titanium bomb, which is called the Φ-factor. Accurately knowing the Φ-factor is challenging because of an absence of reported C_p values for the sample constituents and the constantly changing sample composition and physical state. The inaccuracies of any secondarily derived information such as activation energy (E_a) or the Arrhenius preexponential A would be affected. The Φ-factor used to adjust the self-heat rates is a rough estimate and the adjusted self-heat rates should be considered semi-quantitative. The Φ-factor will not affect the observed onset temperature.

The Φ-factor is calculated using Eq. (1), where C_p is heat capacity and m is mass. For C_p of Swheat and for mixtures containing Swheat, 1.63 J g^{-1} °C^{-1} was used (Ahn et al. 2009).

$$\Phi = 1 + (C_{p(bomb)} \times m_{bomb})/(C_{p(sample)} \times m_{sample}) \text{ (CCPS 1995)} \quad (1)$$

4.3 Test Material Preparation

The materials prepared for testing were simulated waste solutions; the simulated remediated solid phase waste components 3.5 M HNO_3/Swheat and (H,Pb)HNO_3/Swheat; and the remediated simulated liquid waste constituents HTEAN, (H,Pb)TEAN, (H,Pb,Fe)TEAN, HTEAN/Swheat, (H,Pb)TEAN/Swheat, (H,Pb,Fe)TEAN/Swheat, HNO_3/HTEAN/Swheat, and HTEAN/TEA/Swheat. Testing materials were prepared in RPL/507 for DTA/TGA experiments and in RPL/507 and 331/169 for the ARC experiments. The working assumption was that both Pb^{2+} and Fe^{3+} form a metal TEAN. The simulated waste solutions prepared were 3.5 M HNO_3, $Pb(NO_3)_2$-saturated 3.5 M HNO_3, and Fe-saturated $Pb(NO_3)_2$-saturated HNO_3. This section details the methods used to prepare test samples. In addition to the mixtures, the thermal behavior of unscented Swheat Scoop was studied.

4.3.1 Simulated Waste Solutions and TEAN Preparations

The Kolorsafe used was Spilfyter® Kolor-Safe® Sodium Free LIQUID Neutralizer for Acids. A picture of the label is provided in Figure 1.

Limited Distribution

Figure 1. Picture of Kolorsafe used.

To prepare materials representative of components of the liquid waste fraction in Drum 68660, 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 prepared first; next, Kolorsafe was used to neutralize these solutions to prepare (H,M)TEANs; and then Swheat in a 3:1 volume ratio was used to absorb the Kolorsafe-neutralized solutions (Clark and Funk 2014).

The 3.5 M HNO_3 was prepared from UltraPure grade concentrated HNO_3 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; based on Ferris (1960), the [$Pb(NO_3)_2$] will be 0.3 M. The combination $Pb(NO_3)_2$- and Fe- (Pb,Fe) saturated HNO_3 solution was prepared by treating Johnson Matthey Electronics grade 99.2%, -48 mesh iron metal (Fe) powder with the prepared $Pb(NO_3)_2$-saturated 3.5 M HNO_3.

In the neutralization step, the TEA in Kolorsafe reacted with the solution's cations and nitrate to form soluble or insoluble salt(s) of TEAN. To imitate that step, Kolorsafe was used to neutralize the following to pH 7 based on pH paper measurement: 1) 3.5 M HNO_3 to produce HTEAN, 2) Pb-saturated HNO_3 to produce a mixture of HTEAN and lead TEAN [(H,Pb)TEAN], and 3) (Pb,Fe)-saturated HNO_3 to produce a mixture of (H,Pb)TEAN and iron TEAN, [(H,Pb,Fe)TEAN]. As shown in Figure 2, neutralization produced solutions from 3.5 M HNO_3 and Pb-saturated HNO_3, but produced solids from the (Pb,Fe)-saturated HNO_3. For two of the TG/DTA tests, partially and over-neutralized 3.5 M HNO_3 solutions were produced.

To prepare the partially neutralized 3.5 M HNO_3 solution, 0.9 vol part Kolorsafe was added to 1.3 vol parts 3.5 M HNO_3 to produce a 0.8 M HNO_3 and 1.2 M HTEAN solution. To prepare the over-neutralized 3.5 M HNO_3 solution, 1.8 vol part Kolorsafe was added to 0.4 vol part 3.5 M HNO_3 to produce a 0.64 M HTEAN and 1.9 M TEA solution.

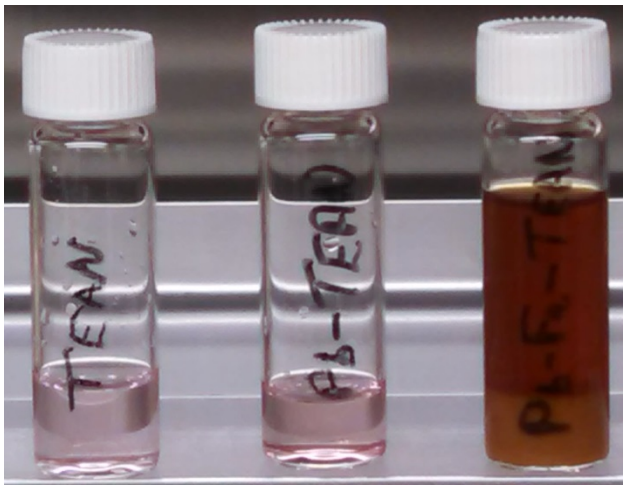


Figure 2. From left to right, pictures of 3.5 M HNO_3, Pb-saturated HNO_3, and (Pb,Fe)-saturated HNO_3, all neutralized to pH 7 with Kolorsafe.

To determine the amount of Kolorsafe required to neutralize nitric acid and metal cation containing nitric acid solutions, the PNNL Analytical Support Operations (ASO) laboratory titrated solutions of 3.5 M HNO_3 and $Pb(NO_3)_2$-saturated 3.5 M HNO_3 with Kolorsafe. The titrations were performed in January 2015 under Analytical Service Request 9725 and WIPP TAT project test instruction 66707-TI-022, *WIPP Technical Assistance – Titration of 3.5 M Nitric Acid and saturated $Pb(NO_3)_2$ dissolved in 3.5 M Nitric Acid with KOLORSAFE®, Liquid Acid Neutralizer*.

The titration curve for 3.5 M HNO_3 is presented in Figure 3a. The equivalence point for 3.5 M HNO_3 was at approximately pH 4. The solution color after the addition of the Kolorsafe was yellow. The measured initial pH levels for the duplicate 3.5 M HNO_3 solutions titrated were 0.52 and 0.62 pH units. The 3.5 M HNO_3 required 1.12 mL Kolorsafe for neutralization, indicating the concentration of the active Kolorsafe ingredient was 3.1 meq/mL Kolorsafe compared to the nominal 3.8 M TEA content in Kolorsafe based on the Material Safety Data Sheet.

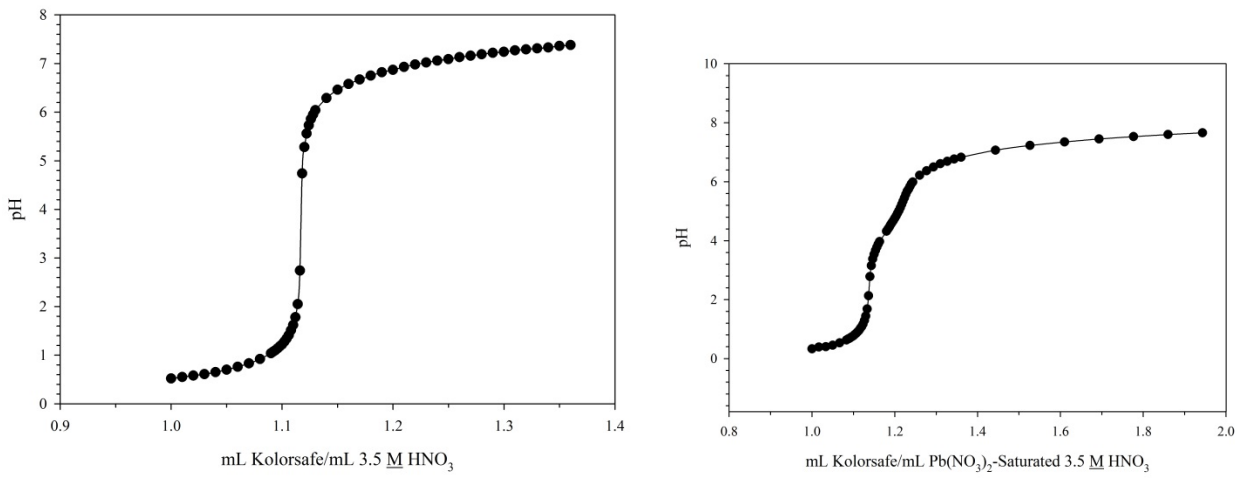
The titration curve for $Pb(NO_3)_2$-saturated 3.5 M HNO_3 is presented in Figure 3b. The $Pb(NO_3)_2$-saturated HNO_3 had two equivalence points, one at pH 2.5 and the other at pH 5.5; the former is for hydrogen ion and the latter is for the Pb. The measured initial pH levels for the duplicate $Pb(NO_3)_2$-saturated 3.5 M HNO_3 were 0.33 and 0.44 pH units. The solution color after the addition of the Kolorsafe was yellow. The titration of the $Pb(NO_3)_2$-saturated 3.5 M HNO_3 required 1.3 mL Kolorsafe to neutralize the acid and an additional 0.09 mL to neutralize or complex the Pb or 0.3 meq of TEA.

Interpolating Ferris's (1960) data for concentrations in saturated $Pb(NO_3)_2$ and HNO_3 solutions predicts 0.3 M [$Pb(NO_3)_2$] in a 3.5 M HNO_3 solution. Comparison to the titration results indicates that neutralization of 1 mole of Pb requires 1 equivalent of TEA, assuming there is not a second equivalency point at a higher pH. Içbucak, Yilmaz, and Olmez (1996) reported that most of the complexes of TEA with divalent metal ions have octahedral geometry and have a metal-to-TEA molar ratio of 1:2, with TEA acting as a tridentate ligand. These results indicate that TEA, the neutralizing agent in Kolorsafe, will complex or bond to metals in the Drum 68660 wastes.

The titration results indicate that adjusting the pH to 7 requires more Kolorsafe than is necessary to neutralize the [H^+] and the Lewis acid metals to their equivalence points. To adjust the pH from the

equivalence point for 3.5 M HNO_3 to pH 7 requires another 8%. To adjust the pH from the second equivalence point for the $Pb(NO_3)_2$-saturated 3.5 M HNO_3 to pH 7 requires an additional 14% dose. This indicates that the liquid wastes adjusted to pH 7 will contain free TEA in addition to the TEANs.

The titration of the lead solution shows that more Kolorsafe than is needed to neutralize the $[H^+]$ will be required to neutralize the Lewis acid metal cations in the liquid waste fraction. The neutralized liquid wastes in Drum 68660 adjusted to pH 7 would be expected to contain HTEAN, (H,M)TEAN, and free TEA, thereby increasing the fuel burden and the chemical character of the TEANs in the liquid waste fraction.



(a) (b)

Figure 3. (a) Titration of 3.5 M HNO_3 with Kolorsafe and (b) titration of $Pb(NO_3)_2$-saturated 3.5 M HNO_3 [estimated 0.3 M $Pb(NO_3)_2$ (Ferris 1960)] with Kolorsafe.

4.3.2 Swheat Mixture Preparations

For these bench-scale experiments, the mixtures of Swheat and simulated waste liquid were prepared by adding 1 volume of solution to 3 volumes of Swheat to absorb Drum 68660's simulated liquid waste fraction or the salt fraction's residual liquid, with the exception of the overneutralized HNO_3/Swheat or TEA/HTEAN/Swheat mixture that was prepared at a 0.9:1 volume ratio. The Swheat used was Unscented Swheat Scoop Natural Clumping Litter manufactured by Pet Care Systems; the container's label is shown in Figure 4a. To promote sample homogeneity and to minimize particle size effects, the Swheat and Swheat mixtures were powdered with a coffee grinder prior to thermoanalytical testing. Figure 4b provides pictures of as-received and powdered Swheat used for preparing test mixtures.

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(a) (b)

Figure 4. (a) Picture of Swheat container label and (b) picture of as-received Swheat and powdered Swheat used for testing.

In early TG/DTA testing, Swheat was placed into the sample pan and the solution was added. In early ARC testing, the mixtures of Swheat with HNO_3 and the Kolorsafe-neutralized solutions were prepared by first adding the Swheat to the ARC-bomb using a funnel, then adding the liquid to the Swheat, then mixing using a stainless steel rod that would fit through the 6.4-mm sample-container neck. This likely did not produce homogeneous mixtures, although the liquid does transfer throughout the Swheat. Subsequently, the mixtures were dried in the Ar-atmosphere dry box using a variety of methods including under vacuum and heating at 50°C and 100°C; none of these drying methods were very successful, and some may have eliminated some near-room-temperature reactions.

Eventually, drying in the Ar dry box was abandoned for simple passive air drying in the laboratory at room temperature and humidities. Figure 5a through Figure 5d provide pictures of freshly powdered Swheat, freshly prepared 3.5 M HNO_3/Swheat, 3.5 M HNO_3/Swheat that has been dried in air at room temperature for 16 h, and 3.5 M HNO_3/Swheat that has been dried in air at room temperature for 8 days, respectively. The dried HNO_3/Swheat mixture acquired a strong orange color, suggesting a reaction between the Swheat and HNO_3.

(a) (b) (c) (d)

Figure 5. (a) Fresh powdered Swheat, (b) freshly prepared 3.5 M HNO3/ Swheat, (c) powdered 16-h dried 3.5 M HNO3/Swheat, and (d) unground 8-day dried 3.5 M HNO_3/Swheat.

Results of drying 3.5 M HNO_3/Swheat and (H,Pb,Fe)TEAN/Swheat open to air are provided in Figure 6. The 3.5 M HNO_3/Swheat (Figure 5c) loses about 31% of its mass after 8 days of sitting in a laboratory at room temperature (16°C to 18.5°C) at relative humidities (RHs) ranging from 10% to 15%. The original sample was 33.8% H_2O, 7.6% HNO_3, and 59.6% Swheat. The sample appears to be approaching its nominal equilibrium liquid content after 120 h. Assuming the mass loss was due solely to H_2O loss, 90% of the H_2O evaporated. This is a very rough approximation since HNO_3 has a variable vapor pressure depending on the HNO_3 concentration, which gradually increases until the HNO_3 in the liquid phase reaches 15.6 M or approximately 70 wt% HNO_3 and 30 wt% H_2O. By reasonable deduction, the residual liquid in the Swheat would be expected to be highly concentrated in HNO_3.

In comparison, (H,Pb,Fe)TEAN/Swheat drying under similar conditions at room temperature but with RHs ranging from 10% to 21% dries to its equilibrium water content in about 80 h (see Figure 6). The 21% RH occurred on the last few days of drying, but the higher RH does not appear to have significantly increased liquid content. Unfortunately, there is no basis for estimating either the water or acid content in this starting mixture. (H,Pb,Fe)TEAN appears to permit the Swheat to dry more quickly than the HNO_3.

These two Swheat drying profiles indicate that when fully exposed at room temperature to RHs ranging from 10% to 20%, Swheat could dry to its equilibrium liquid content in 3 to 10 days. Extrapolation to behavior in a TRU-waste drum depends on a number of physical and chemical factors, including the composition of the absorbed solution, the amount of air circulation, the environmental temperature and RH, the hygroscopic nature of any associated chemicals, and the temperature of the Swheat mixture.

Limited Distribution

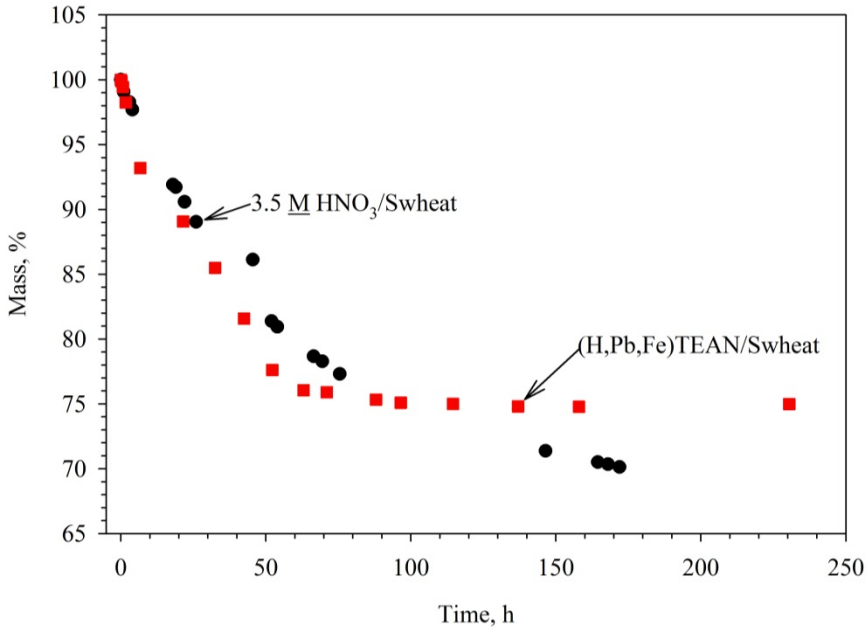

Figure 6. Drying profiles for 3.5 M HNO_3/Swheat and (H,Pb,Fe)TEAN/Swheat in room temperature air with RHs ranging from 10% to 20%.

Early testing of Kolorsafe-neutralized surrogate liquid wastes used as-received Swheat rather than the ground or powdered Swheat. Figure 7a and Figure 7b a provide pictures of large-grained and powdered Swheat with HTEAN sorbed.

(a)

(b)

Figure 7. (a) Kolorsafe-neutralized 3.5 M HNO_3/as-received Swheat and (b) Kolorsafe-neutralized 3.5 M HNO_3/powdered Swheat.

To observe any reactions that might occur after wastes have dried and to remove the confounding effects of water, a variety of approaches were attempted to remove volatile liquids that would prevent or confound observation of exothermic reactions below 110°C. Some of these methods included drying the sample already in the bomb at room temperature in an Ar dry box, heating the sample to 50°C in the Ar dry box for 4 to 16 h, heating the sample to 100°C in the Ar dry box for 4 h, and mixing the sample and allowing it to dry in a weigh boat such as the one seen in Figure 4(b). The approach used is provided in the discussion of specific experiments.

For the first ARC test, Swheat was added to the container and then HTEAN was added and the mixture stirred in an Ar glovebox. For the next six experiments, reactants were weighed out and thoroughly mixed together to promote complete homogeneity. For these early experiments, all reactants were degassed and brought into an Ar-filled glovebox prior to preparation. Mixtures were then packed

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into the bomb and the total mass measured once more. For the last three ARC experiments, the samples were passively dried in room temperature air and then packed into the ARC container. The sample containers were then securely tightened to the pressure measurement line, which was purged and refilled with silicon oil prior to each test.

5.0 Thermal Analysis Testing Results and Discussion

The thermal sensitivities and behaviors of several simulated major constituents of the MIN02 wastes were measured using simultaneous TG/DTA in Ar or air and ARC. The heat changes as measured by DTA results are presented in terms of ΔT or temperature difference in μV between the sample's and reference's thermocouples. The TG results are presented in arbitrary units roughly based on the percentage of the original mass and the mass change rate in arbitrary unit change per minute as measured by the uncalibrated TG. The ARC-measured self-heat rate in °C/min, pressure in bar, and pressure change rate in bar/min are provided as a function of temperature using an Arrhenius scale but are labeled in degrees Celsius.

Plotting the log of the self-heat and pressure change rates vs. Arrhenius temperature effectively provides kinetic and, thus, mechanistic information. For a two-component reaction

$$a[A] + b[B] \rightleftarrows AB \tag{2}$$

$$rate = k[A]^a[B]^b \tag{3}$$

$$k = A\exp(\frac{-E_a}{RT}) \tag{4}$$

where in Eq. (2) and Eq. (3), A and B are the reactants, AB is the product, a and b are the reaction coefficients, and k is the reaction rate constant. In Eq. (4), k is again the rate constant, A is the Arrhenius preexponential or frequency factor, E_a is activation energy, R is the gas constant, and T is temperature. For easier interpretation of the ARC self-heating and pressure change rate results, the data are plotted on an Arrhenius scale. The spacing between successive temperatures is provided by the Arrhenius temperature transform presented in Eq. (5):

$$Arrhenius\ T = 1 - [\frac{273.15}{273.15+T}] \tag{5}$$

When log rate data are plotted against an Arrhenius temperature scale, the slope is E_a and the intercept is A. Thus, linearity indicates a single mechanism and deviations from linearity imply a change in mechanism upon reaching a higher temperature.

5.1 Thermal Behavior of Swheat

Swheat is generally stable between room temperature and 100°C, but can be oxidized by air (Jenkins et al. 1998), and thus contributes to the overall thermal runaway event in Drum 68660. To understand a chemical system and to remove confounding factors, it is valuable to understand the thermal behavior and properties of the individual components. For that purpose, the thermal susceptibility of Swheat was investigated using only TG/DTA in both Ar and air. The former provides information on the behavior in

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anaerobic conditions and the internal stability of materials. The latter provides information on the material's susceptibility to an attack by oxygen in air.

Figure 8 provides the DTA-measured thermal differences, ΔT in μV, between thermocouples in contact with the sample and reference material (alumina) and the TG-measured mass in arbitrary units and the mass change rate in arbitrary units min^{-1}. The TG/DTA indicates that an endothermic mass loss reaction, which is likely water evaporation, begins immediately and, based on the TG, ends near 150°C when heated at 5°C/min. The mass and mass change curves indicate that a second monolithic decomposition reaction begins shortly after the first, also near 150°C. The DTA indicates that this decomposition reaction is not a simple endothermic reaction; rather, there may be multiple steps that have little effect on the decomposition rate. The different constituents in Swheat may decompose slightly differently. Alternatively, the decomposition may proceed with a series of exotherms occurring simultaneously with a larger endotherm. Analysis of the gases evolved during the TG/DTA experiment by infrared spectroscopy or mass spectrometry could assist in understanding the cause of the erratic DTA results.

The high temperature water loss is not surprising given the affinity of glucosidic materials for water and the molecular distribution of water across the glucose polymer (Child 1972). This illustrates the strong bonds between water and the organic kitty litter, but it also illustrates that water can be removed from Swheat over time. The water content is likely controlled by equilibrium and physical conditions such as air movement or breathing through a waste drum's vent.

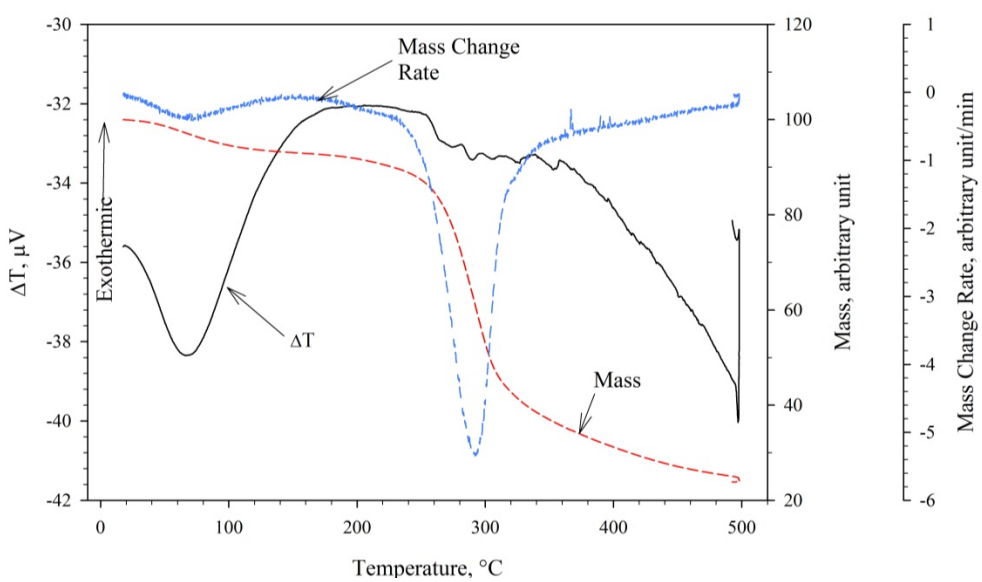

Figure 8. Thermal behavior of undried Swheat in Ar as measured by TG/DTA at 5°C/min.

As shown in Figure 9, Swheat in air also begins an endothermic reaction as soon as it is heated at 5°C/min from room temperature. The first reaction (endothermic) is likely due to water loss and ends near 150°C, and the second reaction (exothermic) begins immediately after the end of the first reaction. The shoulder on the DTA curve near 320°C indicates that a third reaction occurs simultaneously with the second. The onset of the second reaction occurs at the temperature at which the Swheat decomposes, suggesting the susceptibility of the decomposition products to combustion.

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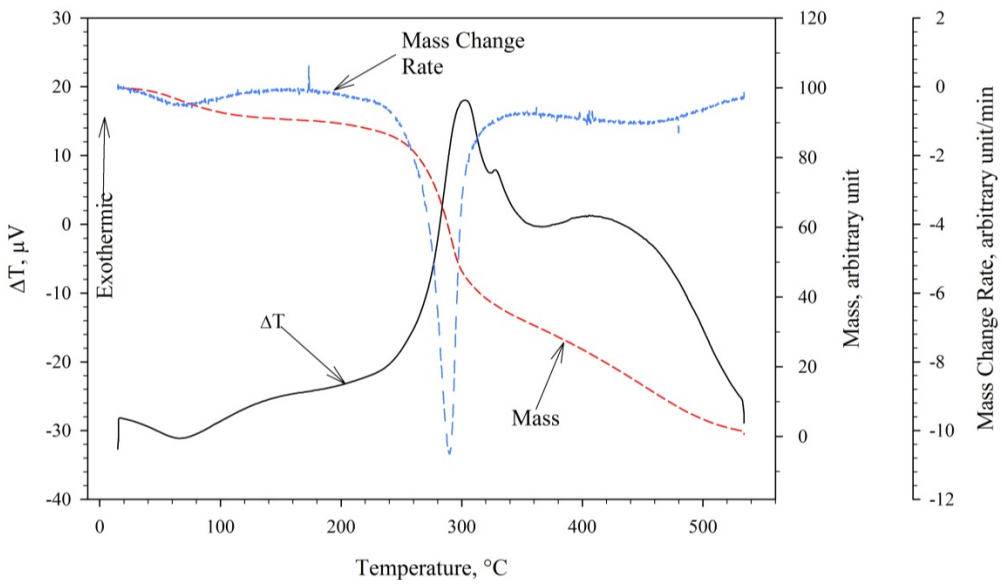

Figure 9. Thermal behavior of undried Swheat in air as measured by TG/DTA at 5°C/min.

These two experiments show that Swheat will decompose in anaerobic conditions or oxidize in air near 150°C if heated at 5°C/min.

5.2 Thermal Behavior of 3.5 M Nitric Acid/Swheat

Swheat with absorbed HNO_3 should represent one portion of the primary reactive components of the salt waste fraction that was placed into Drum 68660. This component should arise as the Swheat absorbs the acidic occluded or interstitial saturated salt solution associated with the nitrate salts fraction. The other waste components are dissolved and undissolved nitrate salts.

To determine the thermal reactivity of this surrogate waste, undried 3.5 M HNO_3/Swheat was analyzed using both TG/DTA and ARC. The "dried" or aged 3.5 M HNO_3/Swheat starting material was used for the ARC to improve the detection of low-temperature reactions masked by the presence of water.

The TG/DTA analysis of 3.5 M HNO_3/Swheat after drying for 3 h at 20°C in Ar is provided in Figure 10. The TG/DTA found the immediate expected endothermic mass loss due to water loss and suspected HNO_3 evaporation. While the water is evaporating, a rapid exothermic reaction starts near 110°C and continues until 140°C. A slower exothermic reaction continues until the experiment is stopped at 500°C. Applying the 100°C CCPS process operating guidance for TG/DTA suggests that the HNO_3 is reacting exothermically with the Swheat at lower temperatures, possibly near room temperature.

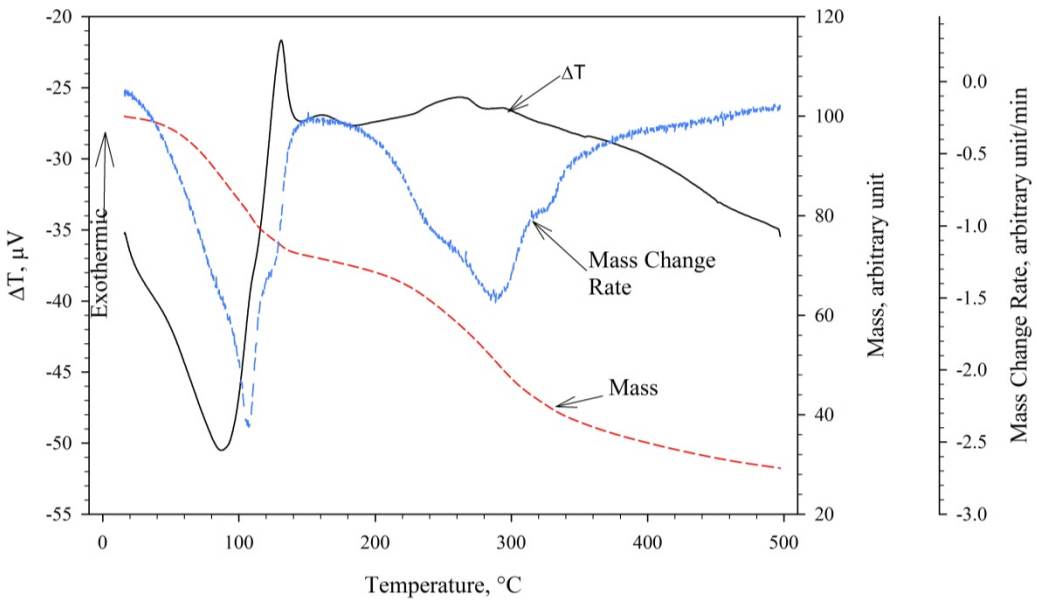

Figure 10. TG/DTA-measured thermal behavior of 3.5 M HNO_3/Swheat in Ar at 5°C/min. Sample dried 3 h at 20°C in Ar.

As Figure 11 shows, the ARC-observed exothermic reaction began immediately after the start of the experiment at 30°C and 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 water evaporation rate, and therefore the reaction was unable 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, when endothermic demands of water evaporating again exceeded the heat production rate required for the sample to continue to self-heat. It is important to recognize that the chemical reaction itself does not stop at this 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 indicates that there is an exothermic reaction between HNO_3 and Swheat near room temperature, but the 2.8-g sample cannot sustain a heating rate of 0.01°C/min below 40°C in the presence of the volatile liquids in the sample. When the sample is heated to 50°C, the reaction rate is sufficient to self-heat to near the boiling point of water. This ARC experiment suggests that, when dry, this mixture would be able to self-heat to temperatures above 160°C.

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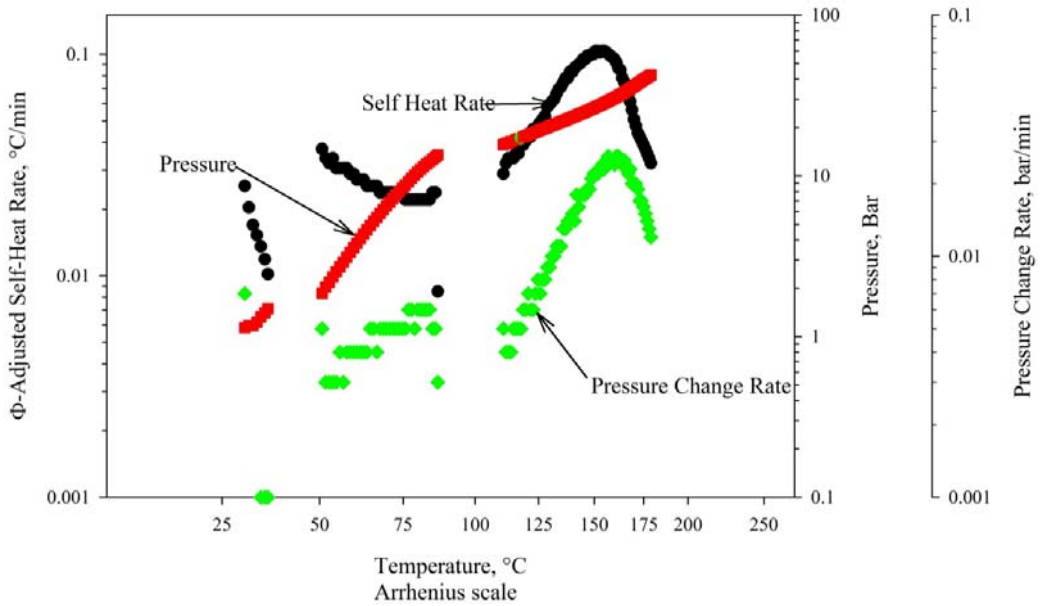

Figure 11. ARC-measured exothermic behavior of 2.8 g undried 3.5 M HNO_3/Swheat.

Figure 12 provides the ARC-measured thermal behavior of 7.5 g of 3.5 M HNO_3/Swheat after air drying overnight at room temperature. The ARC observed a self-heating exothermic reaction that started immediately after the experiment began at 30°C and continued to 80°C, where the ARC observed a rapid increase in self-heat rate, pressure, and pressure change rate. The last realistic measured self-heat rate, pressure, and pressure change rate before rupture were 40°C/min, 12 bar, and 193 bar/min, respectively. The instrument was unable to respond rapidly enough to prevent the reaction from generating sufficient pressure to rupture the sample container. Figure 13a provides a picture of a new sample container for comparison with this experiment's container after the experiment presented in Figure 13b. Since this is an Arrhenius plot with the log of self-heat rate plotted vs. Arrhenius temperature scale (labeled in degrees Celsius), the linearity of the self-heat curve indicates a singular reaction until thermal runaway occurs, which indicates a change in mechanism.

Inspection of the ruptured sample container pictured in Figure 13b shows a rind of material that was on all recoverable pieces of the bomb. The rind was about 3-mm thick and was densified, probably by the rapid gas-producing thermal event. The rind appeared to be principally unreacted material. This would indicate that the rupture of the bomb required less material than the entire sample.

There are complications with comparing the undried (Figure 11) and dried (Figure 12) ARC experiments studying 3.5 M HNO_3/Swheat. The differences in observed behavior could be due to the moisture content or to the undried material having less total sample and less reactants. The moisture content and its evaporation definitely prevented low-temperature self-sustaining reactions, but the fact that it did not thermally runaway was likely due to the smaller amounts of reactants. Another factor could be the consolidation of the sample upon drying, as discussed earlier.

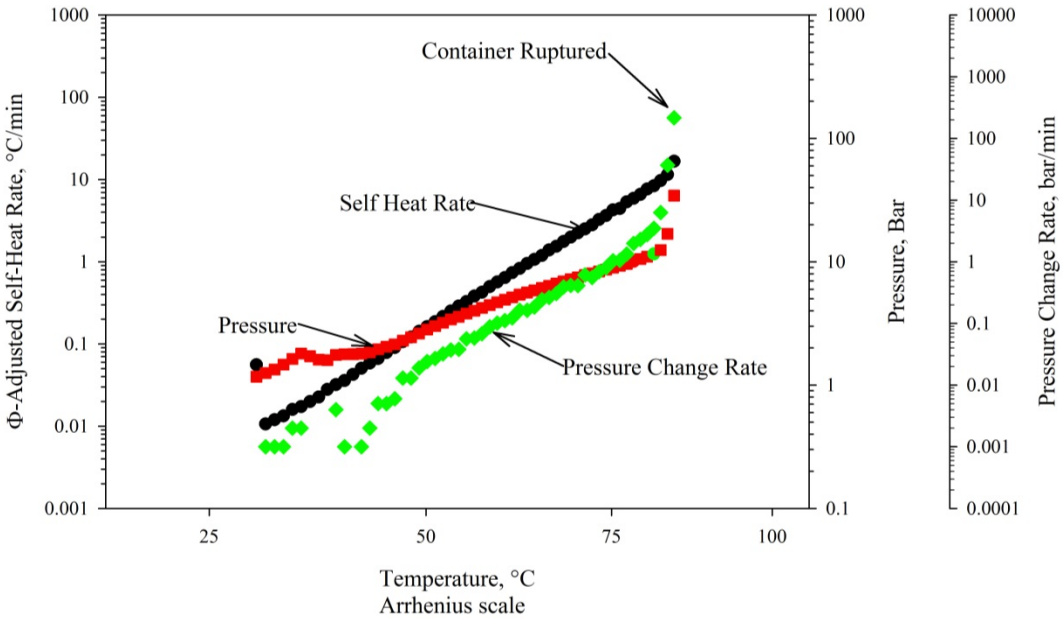

Figure 12. ARC-measured exothermic behavior of 7.5g 3.5 M HNO_3/Swheat dried 16 h at room temperature in air.

The results of an experiment using 7 g of a sample dried in air for 8 days are shown in Figure 13c. The observed onset for a self-sustaining reaction was 40°C rather than the 30°C observed in Figure 12; this difference might be explained by difficulties at the start of the 7-g experiment. The thermal behavior was essentially the same, with the container also rupturing. The ruptured container is shown in Figure 13c.

(a) (b) (c)

Figure 13. (a) New bomb, (b) ARC bomb after 7.5-g 16-h dried 3.5 M HNO_3/Swheat experiment, and (c) ARC bomb after 7-g 8-day dried 3.5 M HNO_3/Swheat experiment.

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Figure 14 compares the self-heat rates measured by ARC for the three 3.5 M HNO_3/Swheat experiments. This comparison illustrates how moisture or a significant heat sink can mitigate or prevent a low-temperature reaction from heating to a temperature where a thermal runaway reaction occurs. Direct comparison is difficult because of differences in the sample size and the amount of reactants. Although possible, the limited test set prevents a determination of whether aging affected the thermal reaction profile through the formation of less stable compounds.

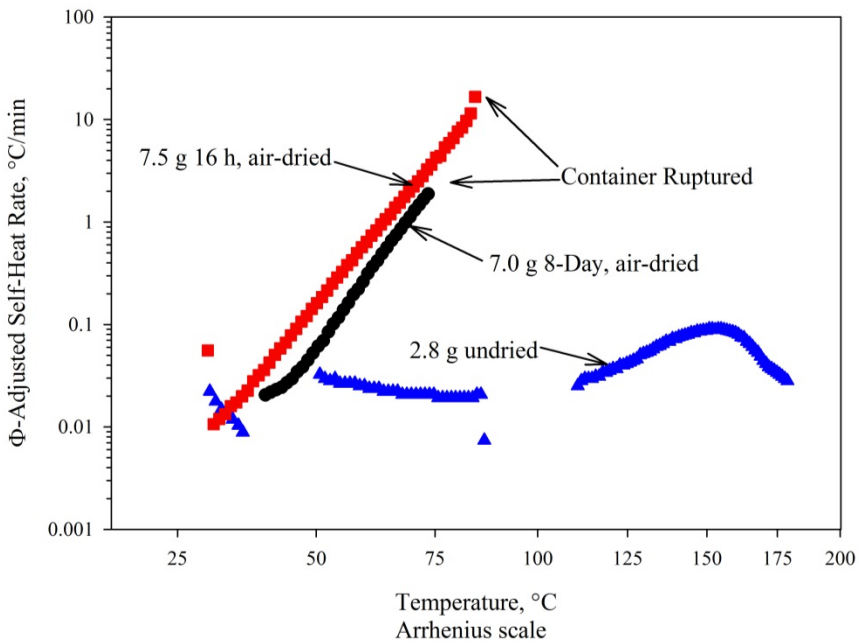

Figure 14. Comparison of ARC-measured exothermic self-heating rates for undried and dried 3.5 M HNO_3/Swheat.

The ARC and TG/DTA experiments indicate that unneutralized HNO_3 will react exothermically with Swheat. These reactions can occur at rates sufficient to heat an undried sample to temperatures approaching the boiling point of water. If dry or aged overnight or 8 days, the mixture is capable of self-heating to a temperature where a thermal runaway occurs.

5.3 Thermal Behavior of (H,Pb)NO_3/Swheat

The addition of $Pb(NO_3)_2$ to 3.5 M HNO_3 increased the complexity and thermal sensitivity of the reaction of HNO_3/nitrate reaction with Swheat. As seen in Figure 15, the dried (H,Pb)NO_3/Swheat begins to lose mass immediately, with some suggestion in the DTA curve of a small exotherm between 35°C and 80°C; supplemental analysis of the evolved gases could help ascertain whether there is an oxidation/ reduction reaction in this temperature range. Beginning at 100°C there is a strong exotherm followed by a second strong exotherm at 110°C. Two exotherms follow, with one between 155°C and 185°C and the second, much larger, one based on the mass loss and mass change rate between 185 and the end of the experiment at 500°C. The (H,Pb)TEAN/Swheat for the TG/DTA experiment was dried in the instrument for 4 h in flowing Ar at 20°C.

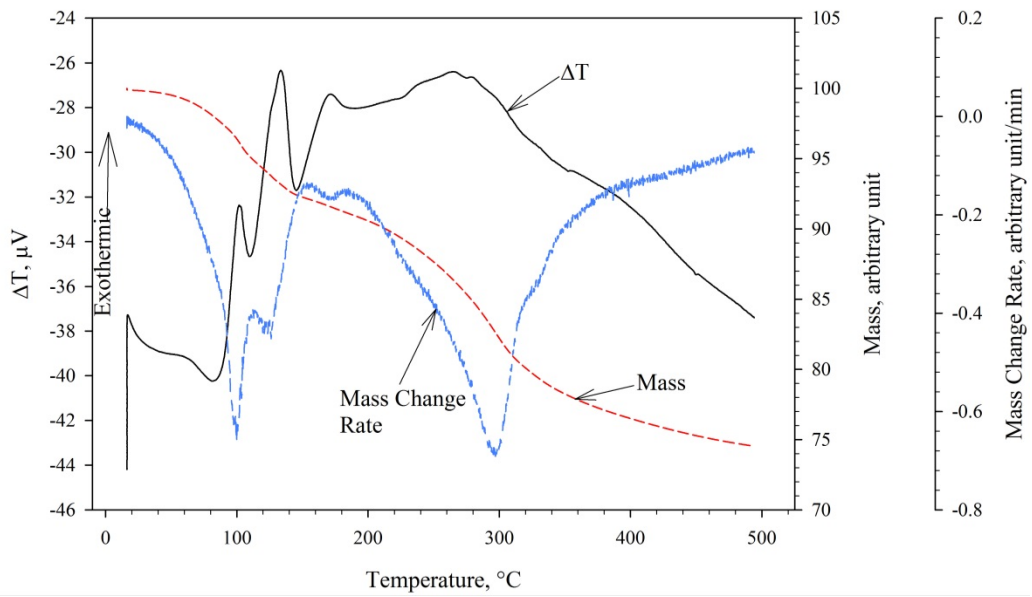

Figure 15. Thermal behavior of (H,Pb)NO_3/Swheat in Ar as measured by TG/DTA at 5°C/min. Dried for 4 h at 20°C in Ar.

Compared to 3.5 M HNO_3/Swheat, the addition of $Pb(NO_3)_2$ caused a new possible reaction between 35°C and 85°C, with the new reaction starting at 100°C. These results indicate that MIN02 metals, at a minimum Pb, lower the reaction onset temperature between nitrate and Swheat and introduce new, more thermally sensitive reactions. An ARC experiment of air-dried (H,Pb)NO_3/Swheat is recommended to further identify the effects of added Pb and to determine if Pb reduces the onset temperature of the ARC-observed thermal runaway reaction. Additional studies of the effects on thermal behavior of other MIN02-metal nitrate solutions could provide additional insights into the factors that affect low temperature reactivity of this type of remediated waste.

5.4 Thermal Behavior of HTEAN and (H,M)TEAN

Neutralization of the acid and the metal ions in the liquid portion of the aged MIN02 waste with Kolorsafe will produce HTEAN and, based on the literature and the team's titrations, other metal TEANs. (H,M)TEANs will be major constituents in the neutralized liquid waste fraction. Pb and Fe are reported (Wallace et al. 2014) to be significant constituents in the Drum 68660 waste; therefore, solutions of 3.5 M HNO_3, saturated $Pb(NO_3)_2$-3.5 M HNO_3, and (Pb,Fe)-saturated HNO_3 were neutralized. This section provides the results of the studies on the thermal sensitivities of HTEAN, (H,Pb)TEAN, and (H,Pb,Fe)TEAN as measured using TG/DTA and/or ARC.

5.4.1 Thermal Behavior of HTEAN

HTEAN should be the predominant TEAN produced when the nominal 3.3 M HNO_3 liquid waste is neutralized with Kolorsafe. TG/DTA was used to investigate the thermal sensitivities of HTEAN.

Figure 16 presents the TG/DTA-measured thermal behavior of HTEAN during isothermal drying for 2 h at 40°C in Ar and as it is heated at 5°C/min to 450°C. The figure shows that the rough mass % mass scale has an unrealistic range, which inhibits detailed assessment of the sample's behavior up to the

strong exothermic reaction beginning at 150°C and the explosive behavior that immediately follows at 240°C. Above 240°C, a violent gas-emitting reaction occurs, driving the sample pan downward, followed by erratic mass measurements as the instrument struggles to maintain balance. This experiment demonstrates that when HTEAN decomposes, it produces gases rapidly with great energy.

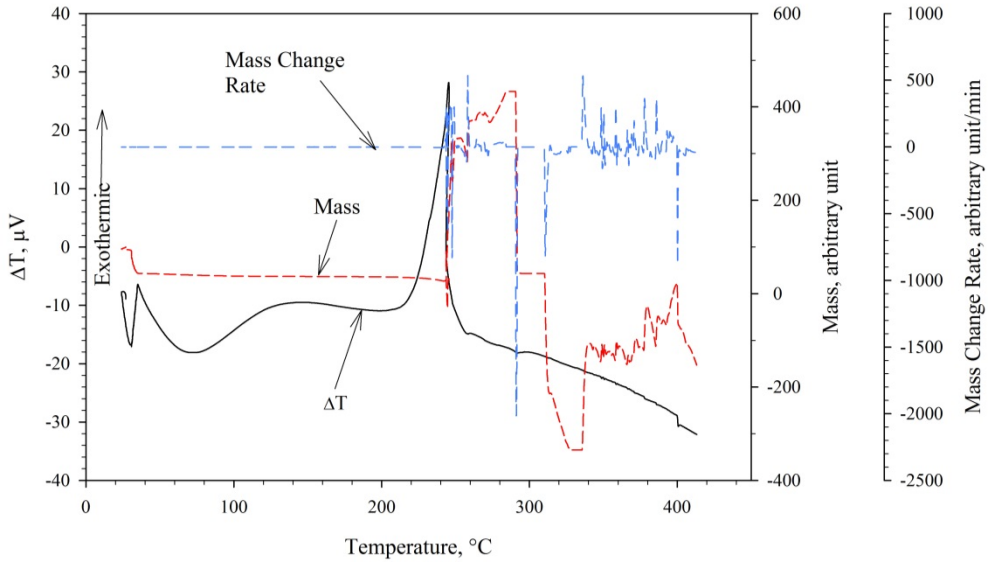

Figure 16. Thermal behavior of HTEAN as measured by TG/DTA at 5°C/min in Ar. Dried at 40°C for 2 h in Ar.

5.4.2 Thermal Behavior of (H,Pb)TEAN

With Pb predicted as being one of the more concentrated metal ions in the aged MIN02 waste, the (H,Pb)TEAN was dried and its thermal behavior was investigated using TG/DTA. The (H,Pb)TEAN was dried at 55°C in Ar for 50 min in the TG/DTA. Metal ions could catalyze the TEAN's decomposition, possibly lowering the decomposition's onset temperature.

The TG/DTA-measured thermal behavior of (H,Pb)TEAN in Ar is presented in Figure 17. The mass and mass-change rate scales are magnified for better observation of reaction onsets as the sample was heated to 55°C for isothermal drying for 50 min and while it was heated at 5°C/min to 500°C. Inspection of the DTA curve finds two very small exothermic peaks at 30°C and 35°C during drying. The DTA peak at 50°C is an artifact of the heating being stopped. After drying, an endotherm that is likely due to water loss begins immediately. Again near 170°C, an exothermic mass loss begins and accelerates near 230°C. During this reaction, a violent, gas-producing reaction occurs at 245°C, ejecting the sample pan. The residual material cocooned the sample pan. The addition of Pb to the TEAN salt does not appear to significantly affect the decomposition behavior of TEAN other than the possible reactions below 50°C.

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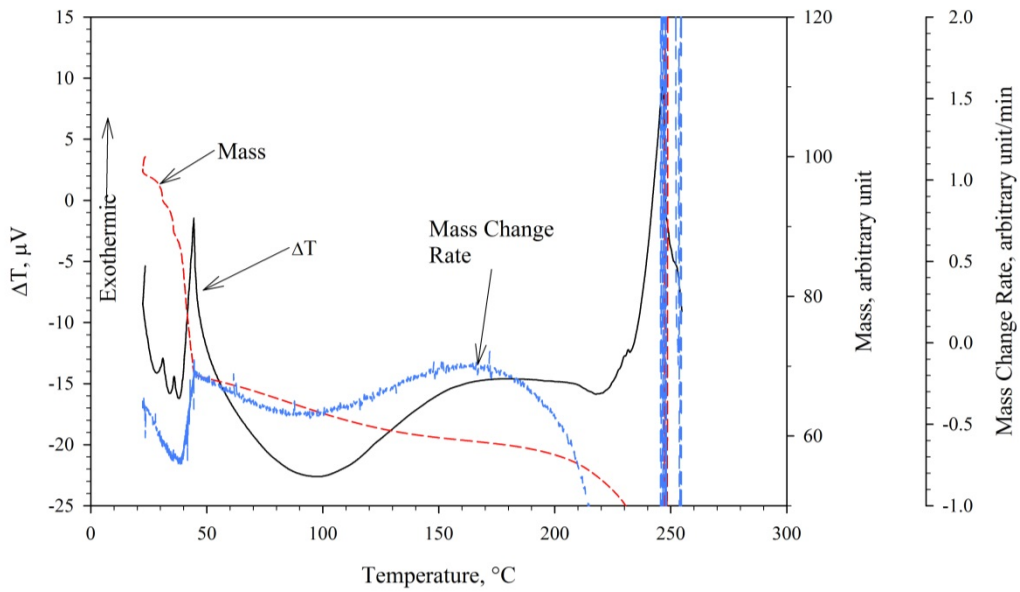

Figure 17. Thermal behavior of (H,Pb)TEAN as measured by TG/DTA at 5°C/min in Ar. Dried at 55°C in Ar for 50 min.

5.4.3 Thermal Behavior of (H,Pb,Fe)TEAN

Because Fe is predicted to be one of the major salt constituents, it may be one of the significant constituents in combination with Pb in the liquid waste fraction. Thus, TG/DTA and ARC were prepared and used to measure the thermal sensitivity of (H,Pb,Fe)TEAN.

The results of the TG/DTA analysis of dried (H,Pb,Fe)TEAN in static air are provided in Figure 18. The (H,Pb,Fe)TEAN was dried for 21.5 h at room temperature in flowing Ar. The (H,Pb,Fe)TEAN in this experiment exhibited a different thermal behavior than both the HTEAN and the (H,Pb)TEAN. Whether the difference is due to the added Fe or due to the use of air rather than Ar is unknown without additional tests.

The (H,Pb,Fe)TEAN exhibits similar behavior with the early endothermic mass loss, presumably due to water evaporation. The first exothermic mass loss begins near 160°C and continues to 200°C, where the mass loss slows. At 215°C, the very rapid reaction begins, although not with the same vigor as the HTEAN and (H,Pb)TEAN. This analysis confirms that the decomposition reaction is a two-step process.

Figure 19 is a picture of the remaining sample after this experiment. The original sample partially filled the sample pan in which the resulting expanded ball is sitting. The residual's metallic appearance suggests that the Pb and Fe were reduced to the metallic state by the TEAN's decomposition. Further characterization is needed to make that assessment.

Inspection of Figure 18 finds some apparent anomalies during the first exothermic reaction with temperatures increasing then cooling. This is caused by the sample temperature increasing faster than the instrument's 5°C/min heating during the reaction and cooling to the instrument's temperature as the reaction slows.

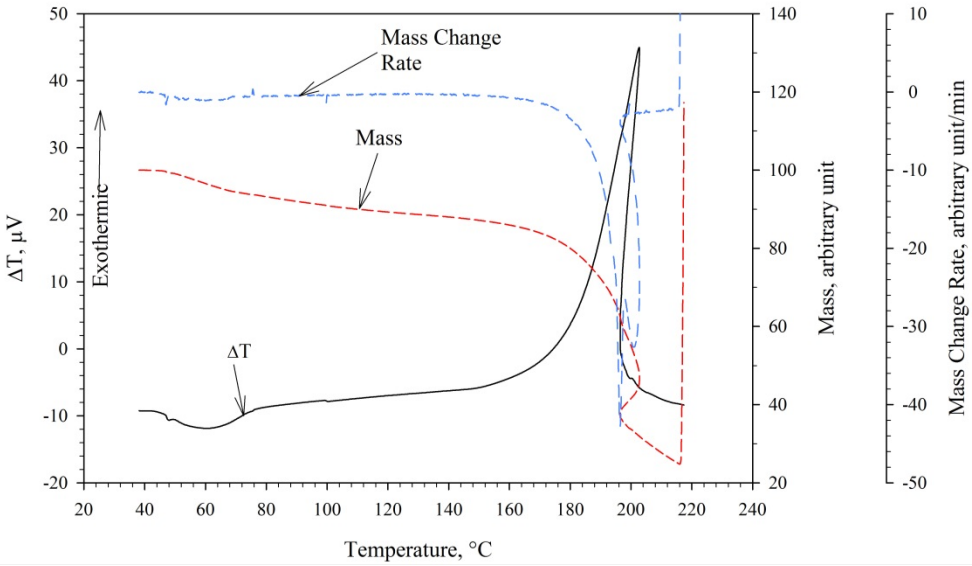

Figure 18. Thermal behavior of dried (H,Pb,Fe)TEAN in static air as measured by TG/DTA at 5°C/min. Dried for 21.5 h at room temperature in flowing Ar.

Figure 19. Picture of residual after TG/DTA analysis of (H,Pb,Fe)TEAN.

The results of the ARC analysis of 3.5 g of dried (H,Pb,Fe)TEAN are presented in Figure 20. The (H,Pb,Fe)TEAN 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. As Figure 20 shows, below 100°C the ARC-observed self-heating rates exceeded 0.01°C/min after the waiting period. However, the self-heating rate immediately fell to negative rates, resulting in only pressure and pressure change rate being displayed in the figure. The ARC believed that it observed an exotherm after each successive 10°C step, with the exception of the 75°C measurement since no heating rates above 0.01°C/min were recorded. The absence of observed low-temperature reactivity could be a result of the drying approach (i.e., drying for 2 h at 40°C to 50°C). 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.

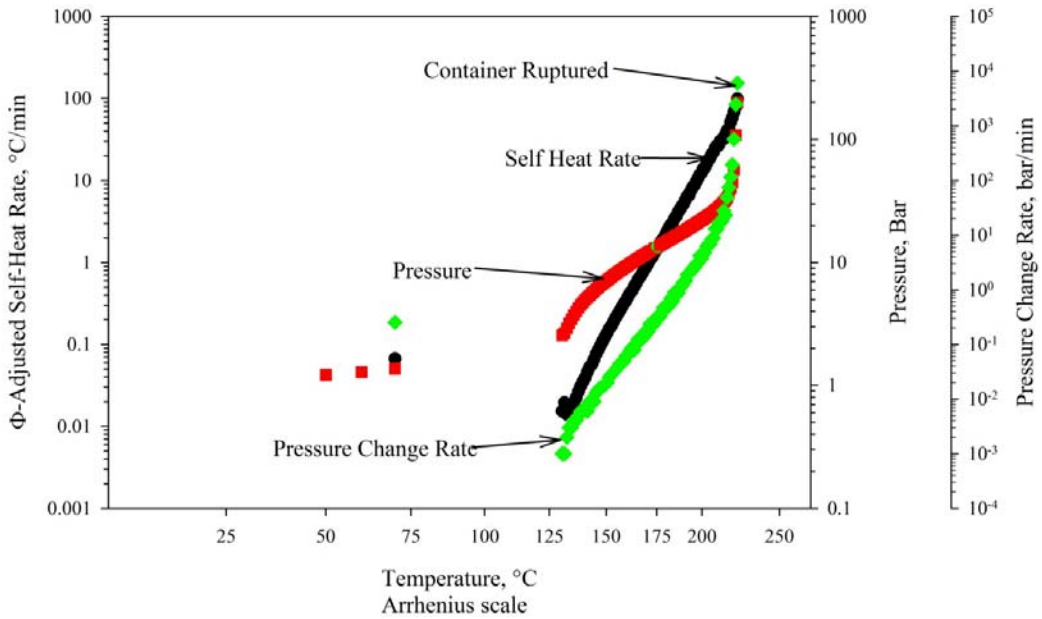

Figure 20. ARC-measured exothermic behavior of 3.4 g semi-dried (H,Pb,Fe)TEAN after drying at 20°C to 50°C for 5 d in Ar.

This ARC experiment confirms the results of all of the TG/DTA analyses of the TEANs, which found significant and rapid exothermic reactions in the 210°C range. This ARC analysis suggests that a TEAN can decompose exothermically at temperatures below 100°C. The analysis also indicates that if heated to 130°C under adiabatic conditions, the TEAN could self-heat to thermal runaway. Applying the CCPS guidance that an operating temperature should be more than 50°C away from the ARC-observed onset temperature, the maximum permitted temperature for (H,Pb,Fe)TEAN is greater than 80°C.

5.5 Thermal Behavior of MTEAN/Swheat

To provide some insights into the thermal sensitivities of a MTEAN and Swheat mixture, TG/DTA and/or ARC were used to study the thermal behavior of HTEAN/Swheat, partially neutralized 3.5 M HNO_3/Swheat (HTEAN/HNO_3/Swheat), and 3.5 M HNO_3 neutralized with an excess of Kolorsafe mixed with Swheat (TEA/HTEAN/Swheat), (H,Pb)TEAN/Swheat, and (H,Pb,Fe)TEAN/Swheat. Although potentially important, the reactions of Swheat with other MIN02 waste nitrate salts (e.g., Ca and Mg) possibly present in solution in the liquid waste were not investigated due to time constraints.

5.5.1 Thermal Behavior of HTEAN/Swheat

HTEAN/Swheat should be the principal component in the bulk of the solidified liquid waste. Its behavior was studied using both TG/DTA and ARC. The TG/DTA samples were dried or partially dried in the TG/DTA while the ARC analysis used an undried sample.

The thermal behavior of HTEAN/Swheat dried at 40°C in Ar for 2 h is presented in Figure 21. The mass loss beginning upon starting the analysis at 80°C appears to be associated with an exothermic reaction that leads into a second exothermic reaction that begins at 150°C and completes near 290°C. The shoulder on the DTA curve indicates another exothermic reaction that starts at 260°C and occurs simultaneously with the second reaction. There is a fourth exothermic reaction beginning at 285°C, just as the large exotherm slows or ends. This fourth reaction appears to continue to near 350°C, although the mass curve indicates continued mass loss. The mass change rate remains constant until 410°C, when another reaction begins; multiple reactions may be occurring simultaneously in this region. The last reaction was incomplete when the experiment was ended at 450°C.

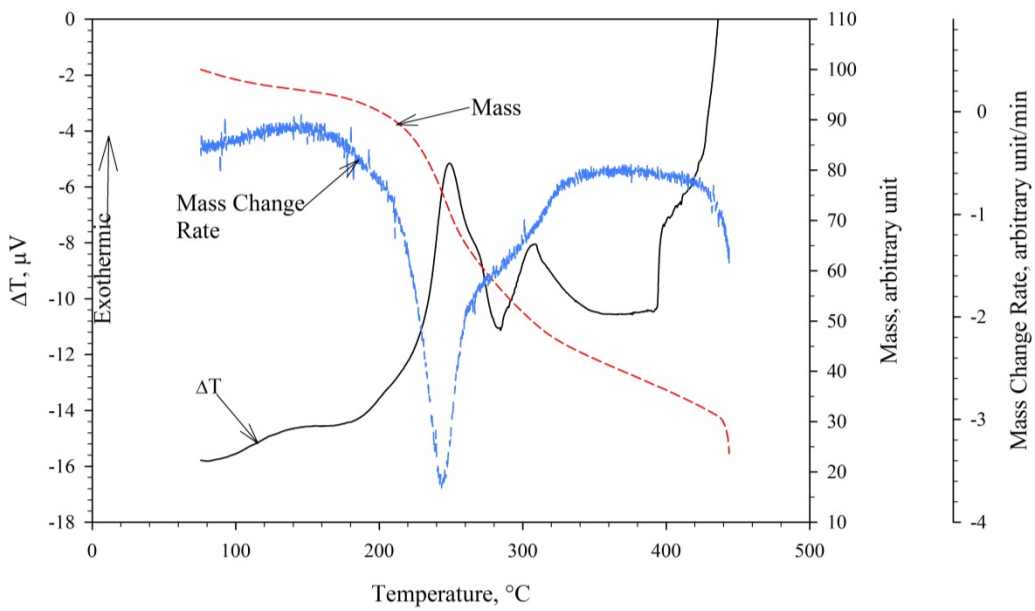

Figure 21. Thermal behavior of HTEAN/Swheat in Ar as measured by TG/DTA at 5°C/min. Sample dried at 40°C in Ar for 2 h.

As shown in Figure 22, the TG/DTA observed a similar general thermal behavior for HTEAN/Swheat as it is heated in air rather than Ar. The sample was dried at 50°C in Ar for 2 h**.** A small exotherm is observed near 60°C below the starting temperature for the Ar experiment. The same reactions occur in the range 100°C to 350°C. At 380°C, the DTA observes another exothermic reaction; however, neither the mass nor mass change rate curves indicate a distinct reaction. Supporting analyses of the off-gases by mass spectrometry and/or infrared spectroscopy would provide insights into whether this is a distinct reaction.

Comparison of the thermal behaviors of the HTEAN/Swheat with its two individual constituents suggests that the combined behavior is more than a simple combination of the two thermal susceptibilities. HTEAN/Swheat is not as kinetically reactive as HTEAN alone which could be because the HTEAN is more distributed and less concentrated. Exothermic reactions are observed earlier for the mixture than for HTEAN, which could be due to nitrate reaction with Swheat or destabilization of the HTEAN permitting earlier decomposition. Significant mass losses occur earlier for the mixture than when Swheat alone begins to decompose.

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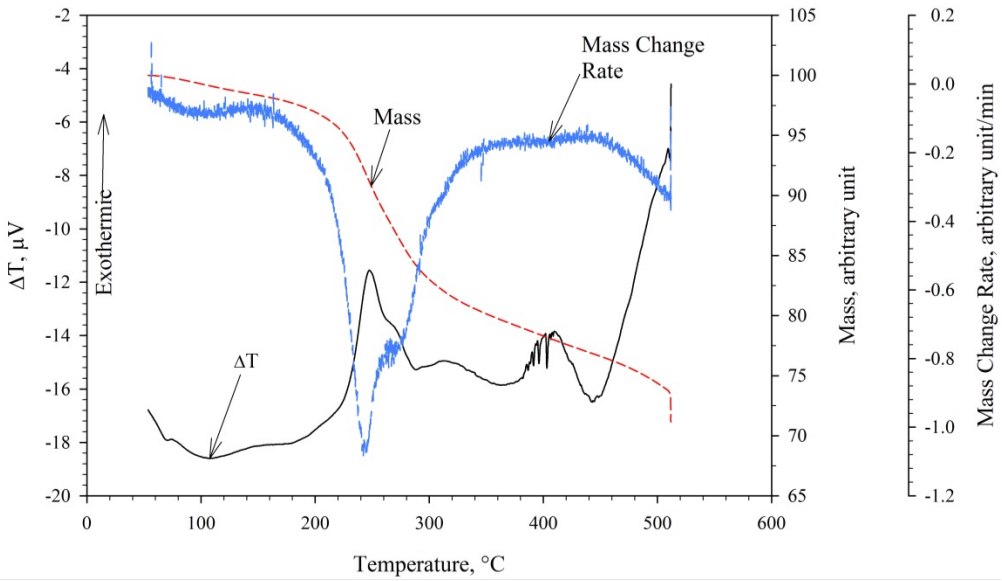

Figure 22. TG/DTA-measured thermal behavior of HTEAN/Swheat in air at 5°C/min. Dried at 50°C in Ar for 2 h.

As shown in Figure 23, the ARC observed no exotherms until the undried sample was heated to 145°C, when a self-sustaining reaction began and continued to 220°C, at which point a second reaction began. This reaction continued to 280°C and was unable to sustain itself. The ARC observed low-grade exotherms above 300°C until the experiment was ended at 320°C. The ARC-observed behavior indicates that the exothermic reactions that occur in HTEAN/Swheat proceed in two steps. In the presence of moisture, the ARC observed no exothermic reactions below 100°C for the 3-g sample.

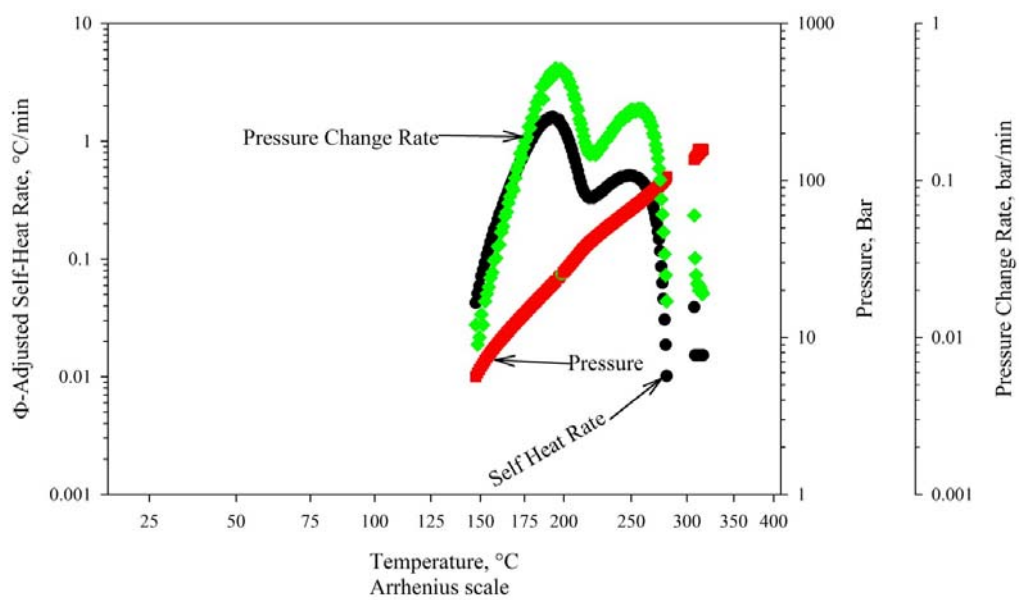

Figure 23. ARC-measured exothermic behavior of 2.8 g undried HTEAN/Swheat.

In summary, the TG/DTA and ARC tests indicate that HTEAN/Swheat is chemically reactive, having the potential for exothermic reactions below 100°C and self-heating reactions above 150°C. There is

insufficient information on the thermal sensitivities to fully assess and understand the thermal sensitivities of this mixture.

5.5.2 Thermal Behavior of HTEAN/HNO_3/Swheat

To investigate the possibility that the liquid waste was not fully neutralized, TG/DTA tests were performed to study the thermal sensitivity of Swheat mixed with 75% neutralized 3.5 M HNO_3 or 1.2 M HTEAN and 0.8 M HNO_3 (HTEAN/HNO_3/Swheat).

As Figure 24 shows, this HTEAN/HNO_3/Swheat, dried for 2 h at 20°C, exhibits the typical immediate mass loss, which is likely due to water evaporation, and then begins to react again exothermically starting near 150°C and ending near 300°C, although the sample continues to lose mass slowly. The 110°C exotherm observed for the 3.5 M HNO_3/Swheat was absent for this acidic mixture. The mass change rate indicates a small reaction, starting at 300°C and ending at 350°C, that occurs simultaneously with the slow mass loss reaction that continues to 450°C or the end of the experiment.

The first exothermic reaction is very similar to the exotherm observed for HTEAN/Swheat. The subsequent reactions observed for HTEAN/Swheat are in general absent, other than the small reaction observed starting at 310°C, which may correspond to the exothermic reaction observed for HTEAN/Swheat starting near 290°C. The primary exothermic reaction peaking at 250°C is much sharper for the HNO_3-rich mixture, but that could be due to the relative shortage of contributing HTEAN decomposition reactions.

Comparison of the TG/DTA-measured thermal behaviors of this partially dried 1.2 M HTEAN/0.8 M HNO_3/Swheat with the undried 3.5 M HNO_3/Swheat (Figure 10) finds significant differences. While 3.5 M HNO_3 has a strong exotherm starting at 110°C, it is not obvious in the partially neutralized acid sample.

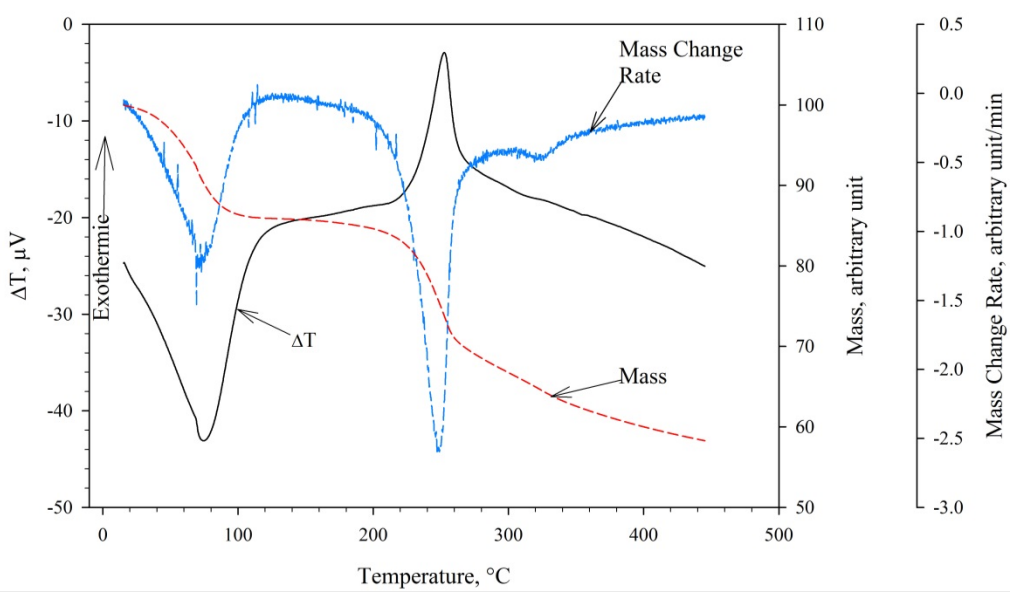

Figure 24. Thermal behavior of underneutralized 3.5 M HNO_3/Swheat in Ar as measured by TG/DTA at 5°C/min. Sample dried at 20°C for 2h in Ar.

Limited Distribution

5.5.3 Thermal Behavior of TEA/HTEAN/Swheat

To investigate the possibility of over-neutralization with Kolorsafe by the waste remediation operators, TG/DTA was used to study a mixture of Swheat and a solution of 3.5 M HNO_3 that had been treated with a four-fold excess of Kolorsafe required to provide a pH of 7 (TEA/HTEAN/Swheat). The sample prepared in the TG/DTA to a 0.9:1 Swheat to TEA/HTEAN solution volume ratio rather than the desired 3:1 ratio was dried in flowing Ar for 3 h at 20°C.

As with the other HTEAN/Swheat mixtures, after the first immediate endothermic mass loss, the HTEAN/TEA/Swheat (see Figure 25) begins an exothermic, gas-producing reaction near 150°C. In contrast to the HTEAN/HNO_3/Swheat, this first exothermic reaction peak extends to 350°C and possibly beyond, peaking at 280°C rather than continuing to 300°C and peaking at 250°C. The TEA-containing mixture has slower reaction kinetics than the HNO_3-containing mixture. This mixture continues to slowly lose mass to 450°C, where the experiment was ended. Addition of a 400% excess of TEA does not affect the onset temperature of the primary exothermic reaction that starts at 150°C, but it does slow this reaction's rate.

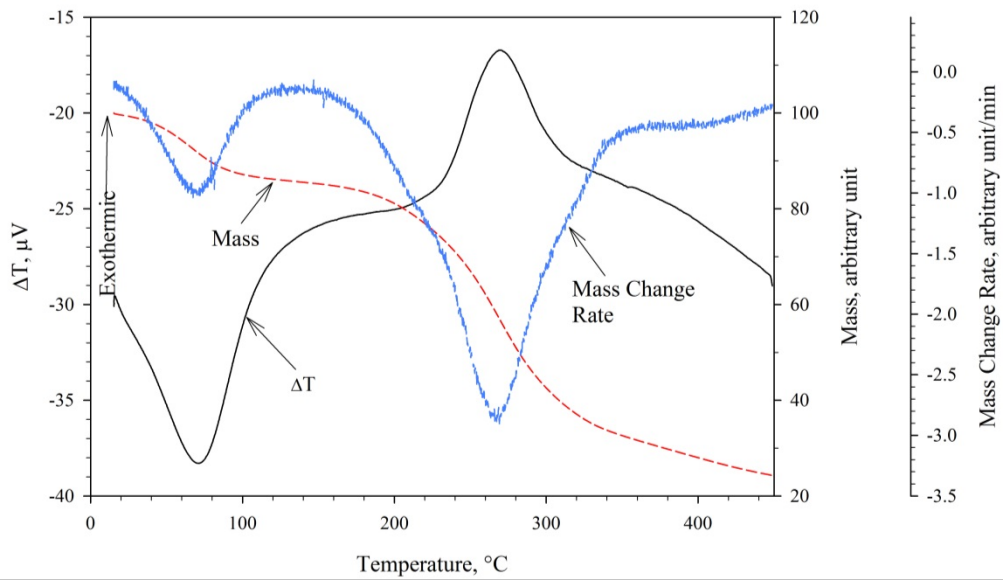

Figure 25. Thermal behavior of over-neutralized 3.5 M HNO_3/Swheat as measured by TG/DTA at 5°C/min. Dried 3 h in Ar at 20°C.

5.5.4 (H,Pb)TEAN/Swheat

The ARC analysis of undried (H,Pb)TEAN found a single indication of exothermic behavior at 30°C as seen in Figure 26. Afterward, any reactions were not fast enough to support evaporation of the water below 100°C and heat the sample. At 145°C, a self-heating exothermic reaction began and continued to 220°C. A second exothermic reaction began at 220°C and continued to 250°C, when the experiment was ended. The ARC analysis suggests the possibility of exothermic reactions below 100°C and indicates that under adiabatic conditions (H,Pb)TEAN will support a self-sustaining exothermic reaction up to 250°C.

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The experiment did not determine the behavior of dried (H,Pb)TEAN, which would eliminate the confounding effects of water evaporation.

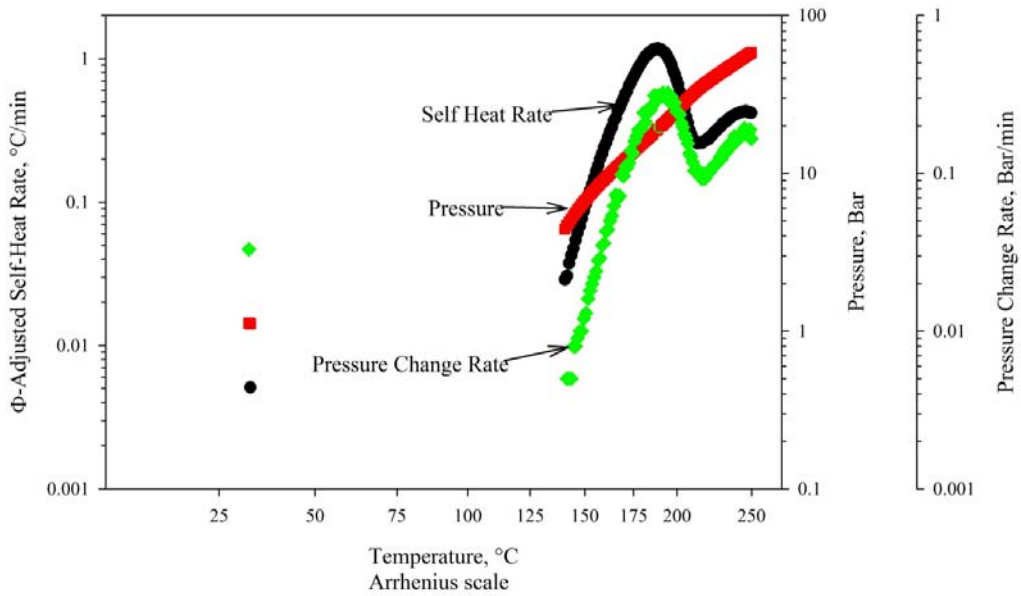

Figure 26. ARC-measured exothermic behavior of 2.8 g undried (H,Pb)TEAN/Swheat.

5.5.5 (H,Pb,Fe)TEAN/Swheat

To investigate the thermal behavior of (H,Pb,Fe)TEAN/Swheat, TG/DTA was used to analyze a room-temperature, 11-day, air-dried sample in Ar and static air, and ARC was used to analyze a 7-g sample dried at 50°C for 5.5 h with air blowing into the ARC sample container. The TG/DTA experiments tracked behavior during both heating and cooling at 10°C/min. To make it easier to interpret the TG/DTA results and to accommodate the significant sample temperature increases that resulted from reaction heat, thermal behavior is presented as a function of time rather than temperature.

When heated in Ar, the 11-day dried (H,Pb,Fe)TEAN/Swheat immediately begins to lose mass, which is likely the residual water (see Figure 27). The ΔT curve provides a weak suggestion of an exothermic reaction beginning near 80°C, but there is no secondary indication from the mass changes. Near 150°C a strong exothermic reaction begins that continues and likely occurs simultaneously with the next very strong and fast exotherm with a peak at 315°C. The broadness of the ΔT peak starting at 150°C is likely due to simultaneous reaction with the next reaction. During cool down, an immediate exothermic peak occurs that is likely a continuation of the reaction observed starting at 270°C. The endotherm observed cool down at 250°C is the likely fusion of a salt.

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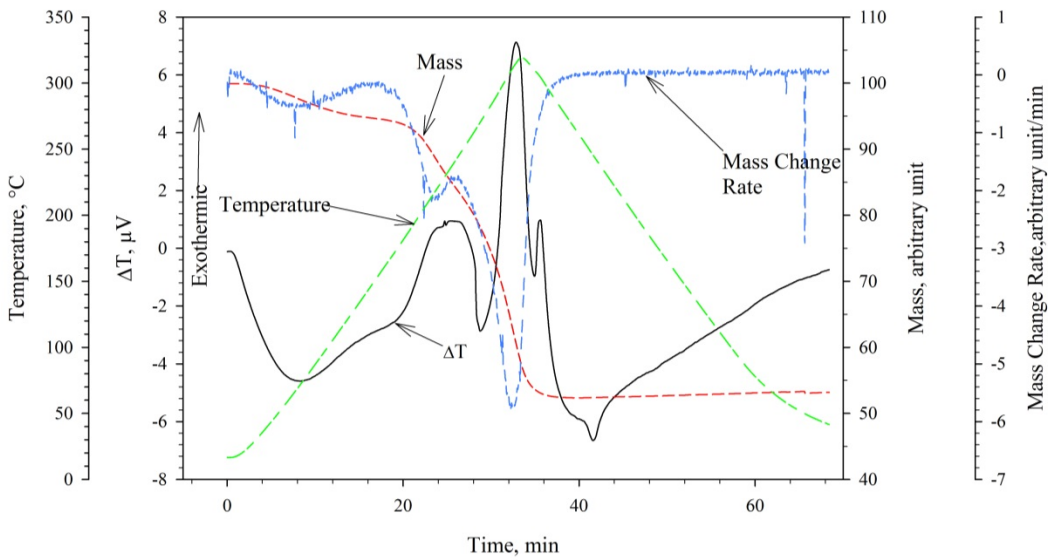

Figure 27. TG/DTA-measured thermal behavior of (H,Pb,Fe)TEAN/Swheat in Ar at 10°C/min as function of time. Dried 11 d at room temperature in air.

The results of the TG/DTA experiment in air are presented in Figure 28 and Figure 29, with the latter providing a contraction of the scales for ΔT and mass change rate to better observe the exothermic reaction that occurs at 90°C and the exothermic shoulder that slows near 235°C as indicated by the mass change rate and the inflection on the ΔT curve. Another shoulder on the ΔT curve suggests yet another exothermic reaction ending at 280°C. The temperature plot shows that the series of exothermic reactions starting near 230°C produce heat very rapidly. The small exotherm observed after the cool down starts is likely due to the heat release being compressed as a result of cooling. The 90°C reaction in air supports that the 80°C exothermic reaction observed for the (H,Pb,Fe)TEAN/Swheat in Ar occurred but it is slower.

These TG/DTA experiments in combination show that (H,Pb,Fe)TEAN/Swheat is susceptible to exothermic reactions initiated by temperatures as low as 90°C. The significant exothermicity in Ar indicates that even if all the available oxygen from air was consumed and anaerobic conditions existed, it would continue to react either through decomposition of the TEAN or by reaction of the nitrate with the Swheat. Additional experiments would be required to differentiate the mechanism.

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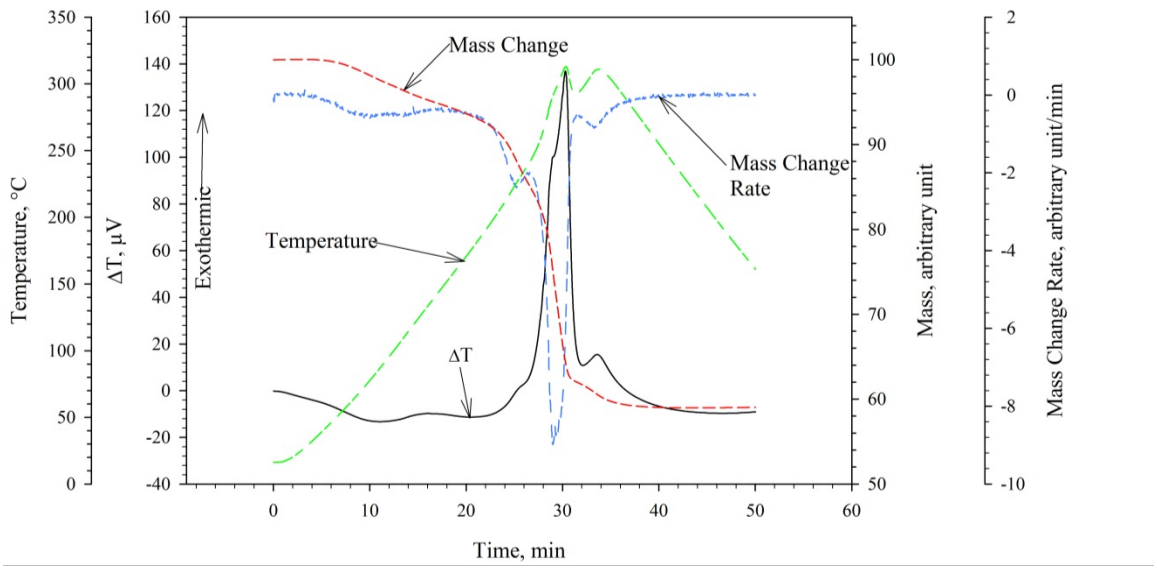

Figure 28. TG/DTA-measured thermal behavior of (H,Pb,Fe)TEAN/Swheat in air at 10°C/min as function of time. Dried for 11 d at room temperature in air.

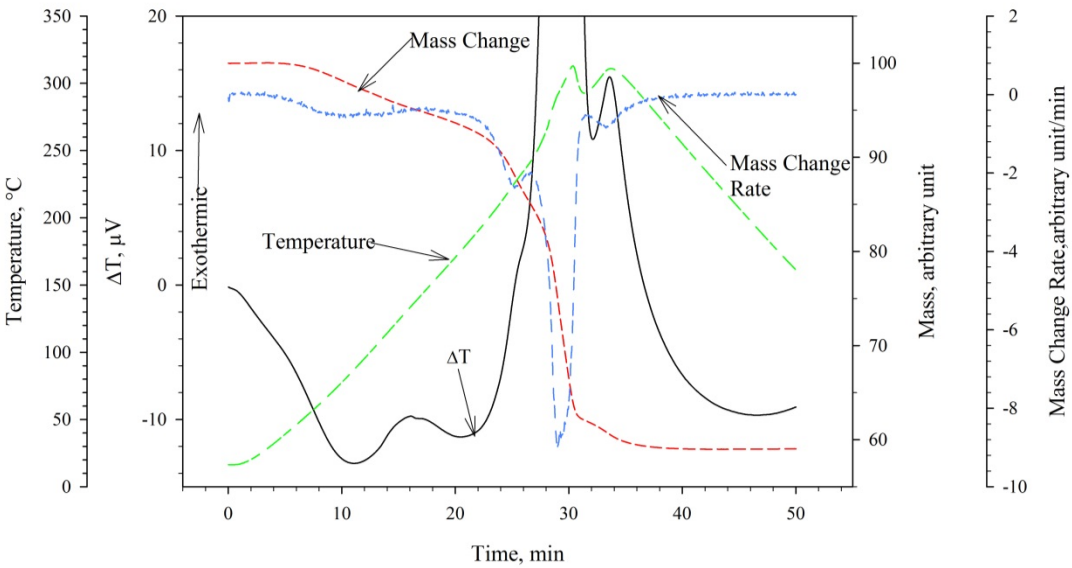

Figure 29. TG/DTA-measured thermal behavior of (H,Pb,Fe)TEAN/Swheat in air at 10°C/min as function of time. Dried for 11 d at room temperature in air.

The ARC experiment provided interesting results, with the container rupturing as a result of a runaway thermal reaction. Figure 30 provides the results of the ARC experiment to determine the thermal sensitivity of (H,Pb,Fe)TEAN/Swheat. The ARC detected heating rates at 45°C and 55°C, exceeding the self-heating rate of 0.01°C/min exotherm criteria, and upon entering the exotherm tracking mode, the heating rate dropped below the exotherm criteria used, likely because the heat production rate was less than the water evaporation rate heat demands. Unsustainable exotherms were detected at 100°C and 110°C, but at 125°C a self-sustaining gas-producing reaction began that self-heated to 210°C, whereupon the reaction accelerated and ruptured the sample container. The final measured self-heat rate, pressure, and pressure change rate were 270°C/min, 170 bar, and 340 bar/min. The sporadic behavior in the

experiment's final moments indicates that a partial rupture occurred before the reaction produced the ruptured container pictured in Figure 31. The linearity of the log self-heat rate vs. the Arrhenius scaled temperature indicates the reaction exhibits Arrhenius kinetic behavior with a singular reaction mechanism until a change in reaction mechanism occurs that ruptures the sample container.

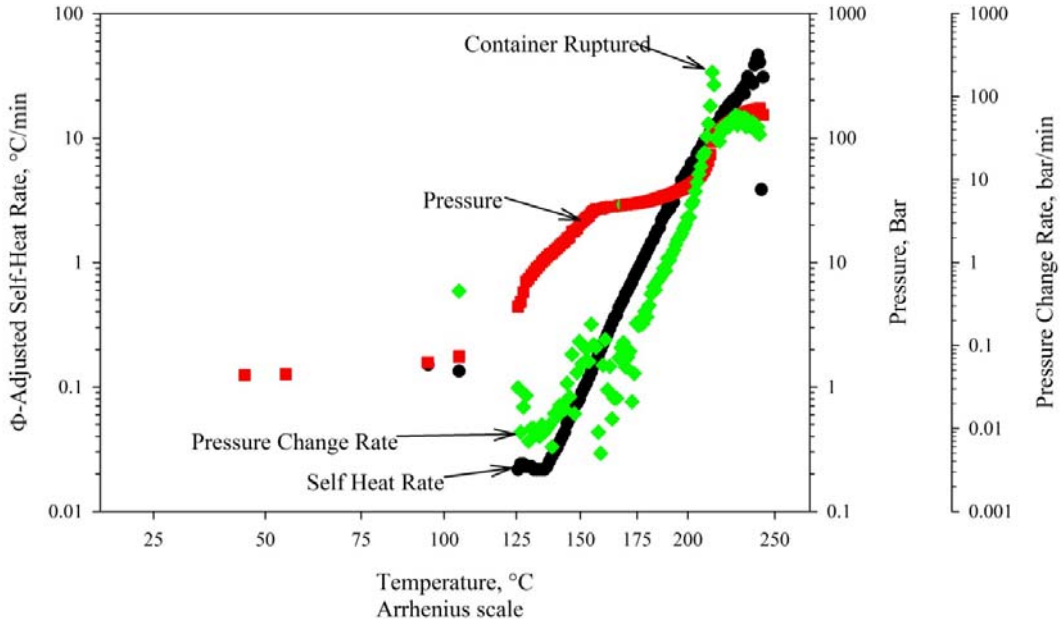

Figure 30. ARC-measured exothermic behavior of 9 g of (H,Pb,Fe)TEAN/Swheat dried at 50°C for 5.5 h in sample container.

The thermoanalytical experiments to determine the thermal sensitivities of (H,Pb,Fe)TEAN/Swheat indicate that this TEAN and Swheat mixture potentially reacts exothermically at temperatures as low as 30°C, but is unable to sustain the reaction and self-heat. It would have been valuable to use the ARC to determine the thermal behavior of the 11-d dried sample but could not be performed due to the project's time constraints. Once a temperature of 125°C is reached, the exothermic reactions that occur will heat the material under adiabatic conditions to a temperature 210°C, where a thermal runaway reaction will occur.

Limited Distribution

Figure 31. (H,Pb,Fe)TEAN/Swheat ARC bomb after analysis.

6.0 Conclusions

Overall, these probative thermoanalytical studies using TG/DTA and ARC show the TRU-waste remediation process used to generate the wastes in Drum 68660 produced thermally reactive individual constituents and mixtures that can react vigorously and energetically produce gases. Some of the compounds and their mixtures are susceptible to low-temperature (less than 100°C) reactions that can self-heat under adiabatic conditions to thermal runaway conditions, while others had ARC-observed exotherms below 100°C that could not sustain a heating rate sufficient to heat the sample, likely because they were overcome by evaporation of water. Others are susceptible to self-heating reactions starting at 125°C or greater that lead to thermal runaway reactions.

Conclusions regarding individual tested materials are as follows:

- 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.
- TG/DTA testing indicated that addition of lead nitrate to 3.5 M HNO_3 reduces the onset temperature of the initial exothermic reaction with Swheat.
- (H,M)TEANs begin to decompose, producing heat and gases, beginning between 125°C and 150°C, and the decomposition reaction(s) become very energetic and very rapid near 200°C.
- Sorption of (H,M)TEANs into Swheat slows the decomposition rate of (H,M)TEANs at temperatures where TEAN decomposes energetically and rapidly.
- Over-neutralization with Kolorsafe alters the thermal exothermic reaction profile and slows the TEAN/Swheat exothermic reaction. ARC testing is needed to assess the effects of over-neutralization.

- Under-neutralization of the acid with Kolorsafe alters the thermal exothermic reaction profile for HTEAN/Swheat by reducing the number of significant exothermic reactions. ARC testing is needed to assess effects of under-neutralization.
- Moisture or liquid content affects ability of reactions of all tested systems to propagate at temperatures less than 100°C.

Because of the limited scope and duration of the probative tests, these findings are not complete enough to adequately assess whether all the tested systems are susceptible to low-temperature thermal initiation when dry. To complete this set of experiments, additional ARC testing is recommended to determine whether the <100°C exothermic reactions observed by TG/DTA for dried (H,Pb,Fe)TEAN/Swheat and by ARC for other partially dried TEAN and TEAN/Swheats would support self-heating for dry materials. Testing using TG/DTA coupled with evolved gas analysis, ARC, and larger-scale testing is also recommended to determine the effects of other aged MIN02 waste constituents on the thermal stabilities of aged MIN02 wastes remediated using Swheat and/or Kolorsafe.

7.0 Quality Assurance

The sample preparation and analysis activities described in previous sections of this report were performed under the quality assurance (QA) program defined in the document *Waste Isolation Pilot Plant Technical Assessment Team Support Project Quality Assurance Project Plan* with an effective date of June 2014. The ASO laboratory participation was performed under their QA plan, ASO QAP-001, Rev. 9, *ASO Quality Assurance Plan*, with an effective date of 5 March 2014, and their existing procedures.

Processes for sample preparation were documented as TIs. These TIs were reviewed and approved by a technical reviewer, a quality engineer, the project manager, and the principal investigator prior to use**.** Completed TIs and supporting data were reviewed by a technical reviewer and a quality engineer, and were then saved as a PDF document ready to be submitted as a project record.

There was one WIPP TAT variance report associated with this work; an uncalibrated balance was used in the 331 building to support sample preparation for the ARC work (66707-TI-021). There were no daily performance checks made as required by the project QA plan. The corrective action was to compare the performance of the balance (Mettler Toledo MS304S with serial number B026046406 in 331/169) with the performance of a calibrated RPL balance (Sartorius ME414S with serial number 22406373 in RPL/405) using a Troemer standard weight set from 331(serial number 4000011206) that was purchased in 2010.

The differences between the two measures using the same weight set were

- 0.0001 g for the 1 g weight,
- 0.0006 g for the 5 g weight,
- 0.0001 g for the 10 g weight,
- 0.0007 g for the 20 g weight, and
- 0.0001 g for the 50 g weight.

The masses weighed during sample preparation ranged from 1 to 30 g, with most masses in the 8 to 30 g range. Thus, the maximum error introduced would be 0.01% for samples in the 1 g range and masses were typically greater than 8 g. The target composition for prepared samples was a nominal 3 volume parts Swheat to 1 volume part liquid with the Swheat volume based on a measured mass with a reported density of 0.55 g/mL. The results only needed to be reported to two significant figures. It was determined that the error introduced by the use of the uncalibrated balance did not to adversely impact the target sample composition.

Project records will be stored using the PNNL electronic records management and storage system (HP Records Manager software) at the completion of the project under project number 66707.

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