Thermochemical Reactivity Hazards of TRU Waste Constituents — 16075

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ABSTRACT

The thermochemical stability of transuranic (TRU) wastes can be problematic and can lead to uncontrolled chemical reactions that can pose a risk to U.S. Department of Energy (DOE) facilities. In 2003, decontamination cloth waste laden with sodium or potassium nitrate and cerium nitrate caught fire in a glovebox at the Rocky Flats Environmental Technology Site (RFETS) in Colorado. In 2005, as a result of the RFETS fire, management responsible for decommissioning Hanford's Plutonium Finishing Plant (PFP) engaged Pacific Northwest National Laboratory (PNNL) to investigate the thermochemical stabilities of potential TRU wastes arising from decontamination of PFP plutonium gloveboxes. Based on PNNL's studies, PFP management used decontamination approaches that would produce TRU wastes that would be stable during PFP waste management operations, during transport, and eventually during disposal at the Waste Isolation Pilot Plant (WIPP) in New Mexico. In 2014, TRU waste containing nitrate-laden organic kitty litter reacted uncontrollably, breached its TRU drum, released TRU, contaminated 21 individuals and the WIPP, and resulted in TRU release outside the facility. In support of the Technical Advisory Team assembled by DOE to investigate the causes of the WIPP event, PNNL investigated the thermochemical stabilities of characteristic wastes in the breached drum and identified a waste that could have caused the breach. This paper describes the RFETS fire, provides results from PNNL's screening studies of potential PFP decontamination wastes and, provides results from PNNL's probative studies investigating the thermochemical stabilities of representative waste constituents in the breached WIPP drum.

INTRODUCTION

The thermochemical stability of transuranic (TRU) wastes can be problematic and can lead to uncontrolled chemical reactions that can pose a risk to U.S. Department of Energy (DOE) facilities. Since 2003, there have been two events that placed DOE facilities at risk. In 2003, there was a fire in a Rocky Flats Environmental Technology Site (RFETS) plutonium glovebox when cloths used to remove a ceric nitrate/nitric acid decontamination solution spontaneously ignited. In 2014, the contents of a TRU waste drum emplaced in the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico, self-ignited, causing the drum to breach and TRU elements to be released to the WIPP and outside the WIPP.

In 2005, in preparation for decommissioning the Plutonium Finishing Plant (PFP) and its gloveboxes, the Hanford Site operator, in light of the RFETS glovebox fire, engaged Pacific Northwest National Laboratory (PNNL) to determine whether TRU wastes arising from candidate decontamination approaches were thermochemically stable at storage, transport, and disposal conditions. PNNL used thermoanalytical

methods to determine the thermal reactivities of decontamination wastes characteristic of 1) cloth wastes arising from the use of aqueous ceric nitrate/nitric acid, 2) wastes arising from using two different gelling agents impregnated with ceric ammonium nitrate and nitric acid [Glygel™ᵃ (Glygel) and Aspigel™ (Aspigel)], 3) and cloth wastes arising from the use of a proprietary decontamination process that employs nitric and hydrochloric acids, complexants, buffering agents, and organic sequestering agents. The results of these studies guided the choice of decontamination method(s) and the strategy for managing the resulting TRU wastes.

In 2014, the DOE chartered the Technical Advisory Team (TAT) to investigate the causes of the TRU waste drum breach at WIPP. In support of that investigation, PNNL used thermoanalytical methods in a probative study to determine the thermal sensitivities of possible waste constituent mixtures. These studies identified at least one possible drum waste component that could explain the self-ignition of drum waste.

This paper summarizes the two ignition events and highlights results from the PNNL studies used to identify a decontamination strategy for PFP plutonium gloveboxes and determine the thermal susceptibilities of wastes in the WIPP TRU drum that breached.

EXPERIMENTAL CONSIDERATIONS

To evaluate reactivity hazards of potential TRU wastes, PNNL applied the investigative approaches and risk evaluation guidelines recommended by the American Institute of Chemical Engineers' (AICHE) Center for Chemical Process Safety (CCPS) [1]. We used the thermoanalytical methods simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) and accelerating rate calorimetry (ARC).

General

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 [1]. 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 [1]. 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.

ᵃ Glygel™ and Aspigel™ are trademarks of Fevdi of France in the United States and/or other countries.

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 rate is roughly proportional to the reactants' concentrations. Impurities can have catalytic effects by reducing E_a (the activation energy), 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.

Test Equipment

To evaluate the thermal susceptibility of tested simulated PFP plutonium glovebox decontamination wastes and simulated characteristic WIPP TRU drum waste materials, we used simultaneous TGA and DTA methods (TG/DTA) and ARC. The TG/DTA provides an initial screen of nominal thermal sensitivities of the reactions that occur and whether the observed reaction 1) loses or gains mass or is stable and 2) is endothermic (requires heat) or exothermic (produces heat). The ARC provides greater thermal sensitivity and is used to identify the onset temperature(s) of self-sustaining reactions and whether ignition occurs.

The TG/DTA-observed thermal behavior of a 10- to 50-mg sample can be complex and can include both endothermic and exothermic reactions. Examples of endothermic events include mass losses due to evaporation of unbound (free) water at temperatures below 110°C for a moist mixture, release of waters of hydration often between 110°C and 140°C, and melting of a compound or eutectic mixture. Examples of exothermic events include mass losses or gains due to the reaction of the sample with an oxidizing or other reactive gas or reaction between oxidizers such as cerium (IV) and/or nitrate with organic material such as cellulosic materials such as cotton cloths or kitty litter made from wheat. The CCPS's chemical reactivity risk assessment rule-of-thumb for differential scanning calorimetry (DSC) results is to consider a system operationally safe if the DSC-observed exothermic reaction onset temperature is 100°C greater than the process operating temperature; DTA is very similar to DSC.

The ARC is an adiabatic calorimeter that provides a more accurate measure of the onset temperature of an exothermic reaction and if the chemical material could support a self-sustaining reaction. We used the ARC in its heat-wait-search mode to observe exothermic behavior in a 1- to 10-g sample in a titanium or stainless steel spherical sample container.

In the heat-wait-search mode, the ARC heats to an operator-selected temperature, equilibrates at temperature (waits), and then searches for sample temperature increases. If the ARC does not see a temperature increase, it heats the sample by

an operator-selected temperature increase and repeats the wait-and-search operation. It repeats this process until it observes a sustainable temperature increase. Then it maintains the calorimeter's temperature at the same temperature as the self-heating sample, thus maintaining adiabatic conditions and ensuring that any heat produced by reactions within the sample goes into heating the sample. The ARC will observe and respond to endothermic events such as evaporation of free water or waters of hydration or melting by reentering the heat-wait-search mode. We typically used 10°C heat steps and an ARC-observed self-heat rate of 0.01°C/min as the criteria for an exothermic reaction. The CCPS rule of thumb for operationally safe operations is an ARC-measured onset temperature greater than 50°C from the operational temperature.

The ARC maintains the oven temperature at the combined sample and bomb's temperature. The additional thermal mass of the titanium bomb, 7 g $\times$ 0.524 J/(g-°C) or ~3.67 J/°C, causes the observed heating rate to be slower than the sample would be by itself. This added thermal inertia is accounted for by multiplying the measured self-heat rate by the so-called Φ-factor calculated by Equation 1.

$$\Phi = 1 + \frac{(C_{p(container)} \; X \; Mass_{container})}{(C_{p(sample)} \; X \; Mass_{sample})}$$ (Eq. 1)

where $C_{p(container)}$ is heat capacity of the titanium bomb. The ARC-measured self-heat rates presented are after adjusting for Φ.

Test Material Preparation

Simulated materials for testing were prepared to support the evaluation of candidate PFP glovebox decontamination wastes and the WIPP drum breach event. PNNL and Fluor Hanford prepared test materials representative of the candidate PFP wastes arising from the ceric/nitric acid decontamination process, the Glygel and Aspigel gel decontamination processes, and the RadPro™ proprietary decontamination process. PNNL prepared simulated wastes representative of both the remediated liquid and nitrate salt wastes that were added to the drum emplaced in WIPP that breached due to internal reactions. The preparation of the tested materials is described in the discussion for each waste type.

DISCUSSION

RFETS Glovebox Fire

The Defense Nuclear Facilities Safety Board [2] reported that in May 2003 a fire occurred in Glovebox 8, Room 2325, Building 371 at RFETS. No staff members were injured as a result of the fire; however, four fire fighters received skin contamination and significant cleanup was required.

Decommissioning of Building 371 began in late 2001. Decommissioning activities included decontamination of RFETS' plutonium gloveboxes. Glovebox 8, located in

the basement of Building 371, was part of an assembly of connected gloveboxes and was used as a dumb waiter to move materials from the ground floor to other gloveboxes in room 2325. In 1986, glovebox 8 was sealed at the basement ceiling using steel and concrete. Glovebox 9 had been removed by the end of 2002 and Glovebox 10 had been decontaminated [2] using 0.25 N cerium(IV) nitrate/1 N nitric acid [3] and removed in January 2003. Glovebox 8 had not yet been decontaminated but contained significant amounts of debris including tee shirts, towels, glovebox gloves, chains wrapped in greasy rags, plastic bottles, three HEPA filters, and a variety of tools [3]. Chemical analysis of the water present after extinguishing the fire found a pH of 5 and 200 mg/L cerium, suggesting that decontamination wastes from other gloveboxes had been left in Glovebox 8.

As described by Beyler [3], the prescribed ceric nitrate/nitric acid decontamination process used at RFETS consisted of spraying 0.25 N ceric nitrate/1 M nitric acid on the surface, wiping the surfaces with cloths, reducing the remaining cerium (IV) to cerium (III) with ferrous sulfate, and neutralizing the residual acid with sodium or potassium hydroxide. Cerium (IV) is a strong oxidant and cerium (III) is not. The belief was that neutralizing the nitric acid rendered the nitrate benign as an oxidant. In practice, the RFETS reduction and neutralization procedure was not strictly adhered to, with the ferrous sulfate put directly onto the wet cloths rather than wringing the liquid from the rags into the container of ferrous sulfate.

The fire started shortly after workers began preparing to decommission the glovebox by using a nibbler to open a large hole in the side of the glovebox by piecewise removal to provide ventilation. The pieces of glovebox wall fell down onto the debris pile. Shortly after workers began to open the box, the fire began. As part of the fire investigation, it was discovered that some of the recovered towels were thermally damaged (black), brown, or white and friable [3]; the recovered towels could include both towels recovered from Glovebox 8 or previously disposed-of waste. Beyler did not observe [3] the pale yellow color that he observed in towels containing ceric nitrate that he ignited in testing to determine the behavior of cloth rags containing ceric nitrate [4]. Beyler [3] concluded that the cause of the fire was indeterminate, but suggested that the most likely cause was impact ignition of nitric acid degraded leaded gloves as a result of cutting operations.

In follow-on studies of the RFETS event and to support the safe use of ceric nitrate for decontaminating DOE facilities, Beyler et. al. [4] used self-heating oven, hot object ignition, radiative smoldering ignition, and flaming ignition/burning rate testing procedures to study ignition scenarios of cerium nitrate soaked 86% cotton/14% polyester cloths. Later, Hartman et. al. [5] reported reactivity results measured by TGA and DSC.

Beyler et. al. [4] later concluded that self-heating is not a hazard for storage scenarios at room temperature (25°C) other than bulk storage depths of several meters (half-thickness 2.6 m). Exposure to hot objects did not cause the cloths to ignite until exposed to 250°C objects on the surface and 230°C buried inside a pile. They observed initiation of smoldering caused by radiant heating at surface

temperatures as low as 175°C. As a result of their testing, they concluded that the presence of cerium increased the thermal sensitivity of the cloths.

Hartman et. al. [5] tested both ceric nitrate and sodium nitrate saturated cloths and observed mass losses starting at 100°C. Using kinetic parameters developed using TGA results, they derived critical cube half-sizes of 37.5 m, 0.54 m, and 0.02 m at 60°C, 100°C, and 140°C, respectively. They also concluded that self-heating at normal storage temperatures is not a hazard other than bulk storage.

As a result of the RFETS fire and because of the uncertainties about the cause, Fluor Hanford Program Management for decommissioning Hanford's PFP engaged PNNL to evaluate the chemical stabilities of TRU wastes produced when using the ceric nitrate/nitric acid process to decontaminate gloveboxes used to process plutonium.

Plutonium Finishing Plant Waste Stability Evaluation

As described by Ewalt et. al. [6] and Hopkins et. al. [7], several different processes were considered for use to decontaminate the plutonium gloveboxes when decommissioning Hanford's PFP. The methods considered were 1) the RFETS ceric nitrate/nitric acid process, 2) the proprietary RadPro™[b] process (see Ewalt et. al. [6] provides the nominal composition), 3) the Glygel gel process which uses ceric ammonium nitrate impregnated in fumed silica, and 4) the Aspigel 100 process which uses ceric ammonium nitrate impregnated alumina.

Each of the resulting PFP-decontamination wastes will contain chemically intimate mixtures of oxidizers (ceric ion and nitrate from the nitric acid, and ceric nitrate or ceric ammonium nitrate) and fuel (rags, ammonium ion, and organic complexants, sequestering agents, and surfactants). Because of the RFETS fire and the potential for chemical reactions between the oxidizers and fuel in the similar candidate decontamination wastes, Fluor Hanford had safety concerns regarding self-sustaining reactions during decontamination operations and during interim storage of the resulting wastes. The storage safety is further compromised on the Hanford Site where temperatures at PNNL's Hanford Meteorological Station have reached a maximum 45°C (113°F) [8]. The higher temperatures can help initiate and accelerate the reactions of the oxidizers and fuel present in the decontamination wastes.

Ewalt et. al. [6] and Hopkins et. al. [7] provide detailed descriptions of how each process would be used to decontaminate a glovebox. In general, for the two aqueous based methods, ceric nitrate/nitric acid and RadPro™, the solution is sprayed on the surface and wiped with a cloth rag or scrubbed with a brush and wiped with a cloth rag. The process is repeated until the target decontamination level is achieved. For the two dry ceric-impregnated gel processes, the prepared gel

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[b] RadPro™ is a trademark of Environmental Alternatives, Inc. in the United States and/or other countries.

is sprayed onto the surface, allowed to dry for 24 hours, and the dried gel is removed by brushing, scraping, or using a hand-held vacuum cleaner.

Aqueous Ceric Nitrate/Nitric Acid Wastes

To evaluate the stability of ceric nitrate/nitric acid wastes, PNNL investigated the thermal stabilities of both cotton/polyester and synthetic cloths soaked in decontamination solution, treated to reduce the cerium (IV) ion to cerium (III) and to neutralize the acid, and then air dried. To prepare the representative ceric nitrate/nitric acid process wastes, we
1) soaked the cloth rag in 0.25 N ceric nitrate/1 M nitric acid,
2) allowed the free liquid to drain from the rag,
3) soaked the drained rag in 0.3 M ferrous sulfate to reduce the residual cerium (IV) to cerium (III),
4) saturated the rag with 2.6 M sodium hydroxide, and
5) air dried the rag in a fume hood.

We also evaluated ceric nitrate/nitric acid soaked rags without ferrous sulfate treatment and hydroxide neutralization.

As Ewalt et. al. [6] reported, PNNL found that the ferrous-stabilized and hydroxide-neutralized ceric nitrate/nitric acid wastes resulting from using 86% cotton/14% polyester cloth wipes were thermally unstable and could begin to react at ambient temperatures, as illustrated in Fig. 1 for 2-day and 13-day old dried cloths.

Fig. 1 shows that the ARC observes exothermic behavior immediately upon starting the experiment at 30°C, but the reaction is unable to sustain itself. However, with subsequent heating additional exothermic behavior is observed. When the sample is heated to 150°C, the reaction can support sustainable self-heating. It is likely that the endothermic evaporation of the residual water prevents the 30°C reaction from sustaining a self-heating reaction. Thus if the cloth waste dried further, the ceric nitrate/nitric acid cloth would support a self-sustaining reaction that could produce significant amounts of gas and raise the temperature to over 450°C. The behavior of the 13-day-old sample indicates that this cloth waste is susceptible to self-sustaining low-temperature reactions. As Ewalt et. al. report, the reactivity of this type of waste should increase with aging to 114 days, but appears to lessen with additional aging based on the behavior of a 146-day-old sample.

We also considered using fully synthetic cloths, 50% polyamide/50% polyester or 20% polyamide/80% polyester, to remove the used ceric nitrate/nitric acid. Our ARC analysis found that air dried, stabilized, and neutralized ceric nitrate/nitric acid soaked synthetic cloths were thermally stable to 170°C and 180°C, respectively, with no indications of low-temperature exothermic reactivities.

Ceric ammonium nitrate/nitric acid gel process wastes

PNNL evaluated the thermal stability of candidate wastes arising from two ceric nitrate/nitric acid gel decontamination processes. The first was Glygel, which used

ceric ammonium nitrate/nitric acid suspended in fused silica and required adding the surfactant *Surfactant TA-96* (diethylene glycol monohexyl ether) just before use to ensure retention of the gel on the surface. The second was Aspigel, which instead used alumina and did not require a surfactant.
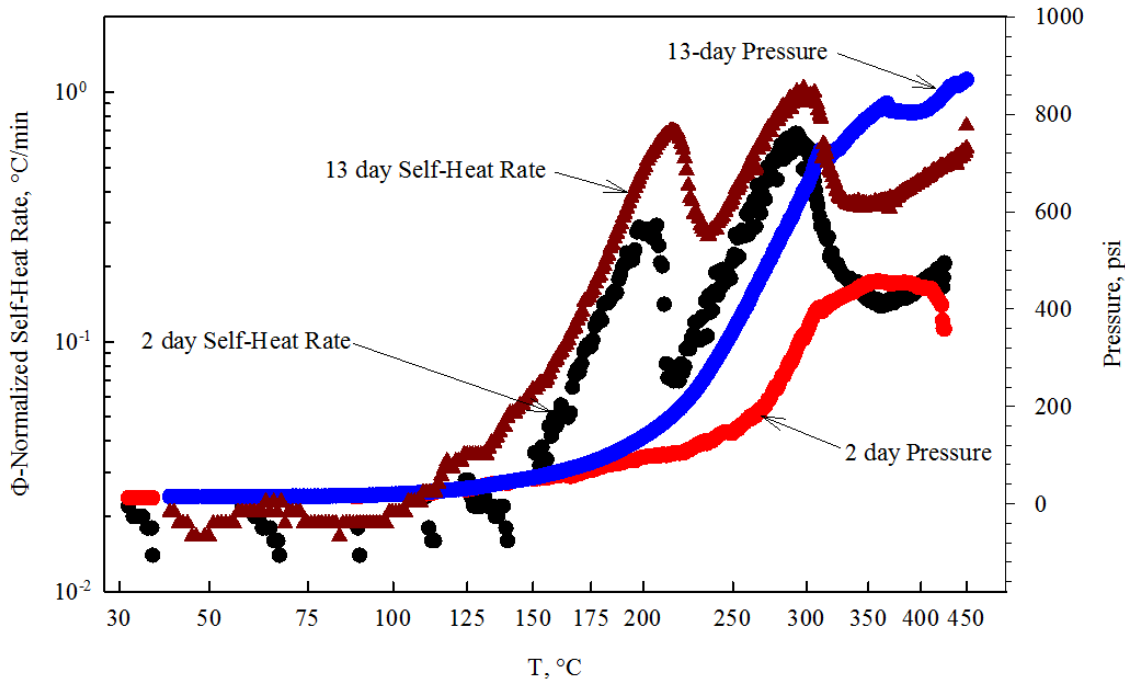

Fig. 1. Arrhenius Plot of ARC-measured thermal behavior of air-dried stabilized ceric nitrate/nitric acid soaked 86% cotton/14% polyester cloth.

To prepare two Glygel process samples, Fluor Hanford
1) degreased the inside of a small stainless steel glovebox with a proprietary degreaser containing <10% sodium hydroxide and < 10% 2-butoxyethanol,
2) sprayed the surfactant and gel mixture onto the walls of the glovebox and allowing it to dry 24 hours,
3) scraped the dried gel from the walls,
4) recovered the dried, spent gel using a small vacuum.

PNNL prepared two additional Glygel samples, one with surfactant and one without surfactant. We freeze-dried a portion of the Glygel with surfactant to assess its behavior after it has dried.

To prepare the Aspigel gel process sample, Fluor Hanford used the same procedure that they used for the Glygel test samples with the exception that no surfactant was used.

PNNL's testing of Glygel found that air dried material began to self-heat at 86°C and that freeze-dried material began to self-heat at 76°C. Glygel was determined to

be too thermally sensitive to be considered for decontamination operations. One test with 3 g of Glygel caused the titanium container to rupture [7].

Our TG/DTA analyses of Aspigel found a significant mass loss below 100°C, which can be attributed to evaporation of retained water. Fig. 2 provides the results of two experiments with recovered Aspigel. With the 3-g sample, the ARC observed a series of unsustainable exothermic reactions starting at about 70°C, which were likely quenched by the Aspigel's contained water; however, after the water has been driven off, the gel supports a self-sustaining reaction starting at about 190°C, or near the same temperature as observed for ceric ammonium nitrate. When the sample was increased to 9.5 g, a self-sustaining reaction began near 75°C; the experiment was stopped at 150°C to prevent thermal runaway. Aspigel also proved to be too thermally sensitive for decontamination operations.
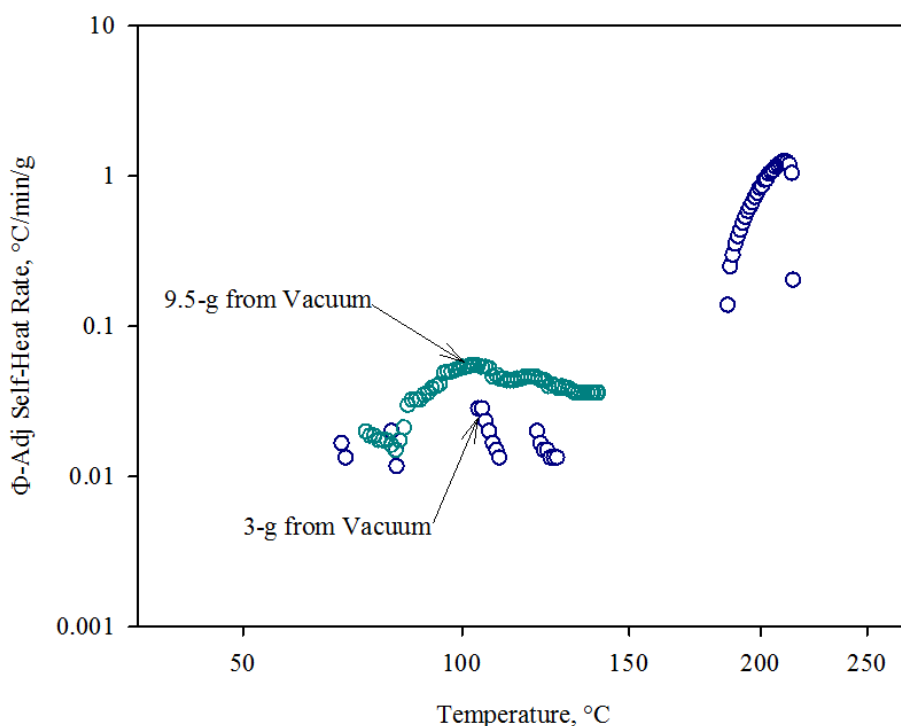

Fig. 2. Arrhenius plot of ARC-measured thermal behavior of Aspigel.

RadPro™ cloth wastes

Another decontamination process considered by PFP was an aqueous decontamination process that employed solutions containing a proprietary mix of acids and complexants as provided by Ewalt et. al. [6].

To prepare the representative RadPro™ decontamination process wastes, we
1) sprayed a 304 stainless steel sheet with a treatment solution,
2) scrubbed the sheet using a brush,
3) wiped the sheet with a cloth rag to saturation,
4) air-dried the rag in a fume hood

As Ewalt et al. report [6], 100% cotton and 20% polyamide/80% polyester cloths soaked with RadPro™ decontamination solution and air dried for 24 h were both susceptible to low temperature reactions below 100°C. As shown in Fig. 3, when 3-day-old RadPro™-soaked cotton cloths were neutralized with sodium hydroxide, ARC-observed onset temperature increased from 70°C to 180°C for the 3-day old material; however, after aging 9 days, the initial ARC-observed onset was ~110°C.
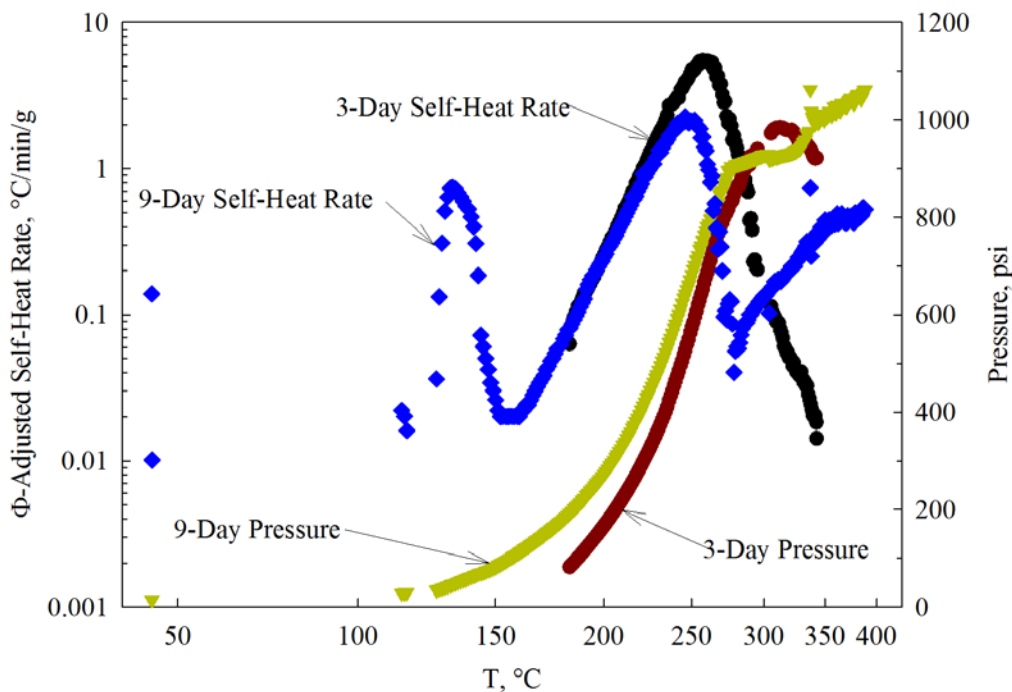

Fig. 3. Arrhenius plot of the ARC-measured thermal behavior of 3- & 9-day air-dried, sodium hydroxide neutralized RadPro™-soaked 100% cotton cloth

WIPP Reactive Drum Waste

In support of WIPP TAT's investigation [9] into the causes of the TRU waste drum breach emplaced in WIPP, PNNL used TG/DTA and ARC to investigate the thermal reactivities of simulated likely wastes put into the waste drum. 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.

According to Clark and Funk [10], the TRU waste in the breached drum contained metal cations, the oxidizing agent nitrate anion, the neutralizing agent Kolorsafe[®][c]

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[c] Kolorsafe is the registered trademark of the NPS Corporation in the United States and/or other countries.

(Kolorsafe), and sWheat Scoop[®d] (sWheat), a wheat-based kitty litter absorbent. Kolorsafe is a pH 10.2 aqueous solution commercial neutralizing agent containing 52.954 wt% of the organic triethanolamine (TEA) (3.87 M TEA) and a pH indicator Alizarin [11, 12]. 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.

Remediation Process, Chemicals, and Materials

To remediate the long-stored waste, first the liquid portion was decanted and neutralized with Kolorsafe, mixed with the sWheat absorbent to absorb the free liquids, and transferred to the drum. Next, the drained nitrate solids were mixed with the sWheat absorbent and transferred to the drum [10]. It is likely that the interstitial liquid remaining in the solids was 3.3 M HNO_3 since the solid waste had originally been washed with 3.3 M HNO_3. Clark and Funk [10] estimate that the sWheat-to-nitrate-salt volume ratio was closer to 1:1 than the targeted 3:1 and the TAT estimates that the sWheat-to-nitrate-salt volume ratio was much lower than the target, at roughly 0.7:1 [9].

Thermal Stability Testing Results

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 the drum. Previous studies at PNNL and by others that determined the thermal stabilities of cellulose and different nitrate salts and amine-based complexants [13-16] helped focus the small test matrix to mixtures of the absorbent 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.

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. 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 $Pb(NO_3)_2$-saturated HNO_3 saturated with Fe. Lead and iron were major metal ions in the wastes. In addition to the mixtures, the thermal behavior of unscented sWheat Scoop[®] was studied.

Drying the sWheat mixtures to remove the complication of the endothermic masking effect of water on the observation of < 100°C exothermic self-sustaining

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[d] sWheat is the registered trademark of Pet Care Systems, Inc. in the United States and/or other countries.

reactions by the ARC proved to be a significant challenge. In the absence of a freeze-drier, we initially prepared test samples in the ARC sample container and then tried to dry the samples in the ARC by gentle heating with and without vacuum; in general, this drying approach was not very successful and introduced additional confounding effects. For the last few experiments, we found that simple air-drying overnight or for a few days produced a very dry mixture. Conveniently, this ambient air-drying approach should be similar to the drying of the liquid waste/sWheat and nitric acid/sWheat components over 70 days of storage in a vented TRU waste drum. These dried sWheat mixtures thus should have water contents similar to those of the drum waste.

During adiabatic ARC tests, two mixtures of 3.5 M nitric acid and sWheat, one dried overnight (see Fig. 4) and the other for 8 days, began to self-heat immediately upon initiation of the experiment at 30°C and 40°C, respectively, with both leading to a rapid, energetic thermal runaway reaction at 80°C with sufficient gas and heat production to rupture the spherical sample container as shown in Fig. 5; 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. For 2.8 g of undried material, the ARC observed two unsustainable self-heating exothermic reactions between 30°C and 40°C and between 50°C and 90°C, followed by a self-sustainable reaction starting at 110°C. The saturated 3.5 M HNO_3/sWheat mixture was used to simulate the portion of the acidic nitrate salt waste fraction arising from sorption of the interstitial solution by sWheat.
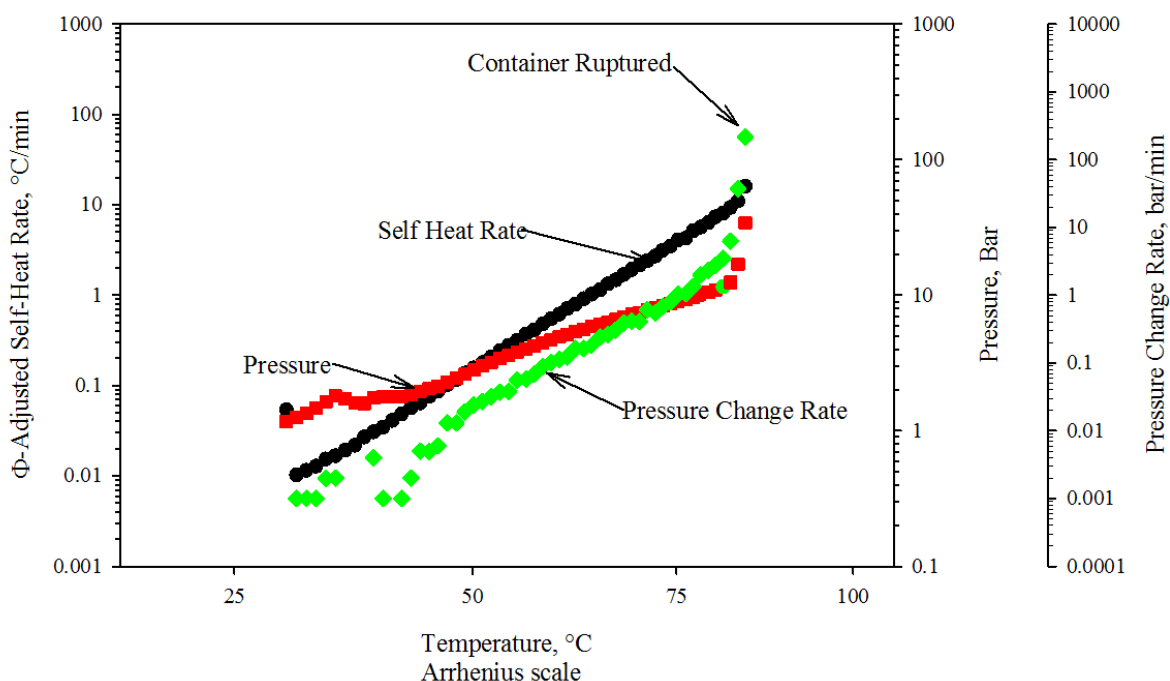

Fig. 4. Arrhenius plot of ARC-measured thermal behavior of 7.5-g 16-h dried 3.5 M HNO_3 saturated sWheat.

Fig. 5. ARC bomb after 7.5-g 16-h dried 3.5 M HNO_3/sWheat experiment.

For partially dried HTEAN, (H,M)TEAN, HTEAN/sWheat, and (H,M)TEAN/sWheat mixtures, which were used to simulate the liquid waste fraction, the ARC observed unsustainable exothermic reactions at temperatures below 100°C and self-sustaining reactions starting at 125°C to 150°C that eventually led to thermal runaway. For wet HTEAN, the sustainable self-heating led to a vigorous and energetic gas-producing thermal runaway reaction beginning near 210°C.

Our TG/DTA testing provided some interesting insights on the effects of added metal cations on waste reactivity. Addition of waste constituent 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. Dried hydrogen, lead, and iron TEAN [(H,Pb,Fe)TEAN]/sWheat in air began reacting exothermically at temperatures less than 100°C.

CONCLUSIONS

Multiple waste evaluations and waste events have highlighted the importance of evaluating the chemical stabilities of possible wastes arising from decontamination and waste remediation operations. Radiological release events have occurred when in-process decontamination cloth waste management practices and waste remediation processes were not rigorously evaluated before their use with respect to waste packaging. The events involving two different TRU wastes highlight the importance of evaluating all phases of waste management during waste generation, packaging for disposal, interim storage, transport, and eventual emplacement in the waste disposal site. In contrast, the experience at PFP where the thermochemical stabilities of decontamination processes and their wastes were evaluated prior to implementing the process and waste packaging provided a stable operational and waste management approach.

PNNL successfully used small scale TG/DTA and ARC to determine the thermal sensitivities of simulated TRU wastes helping to establish safe operating and

storage approaches. This success highlights the benefits of using combined TG/DTA and ARC evaluations to

- determine the thermally-initiated reactivities of potential TRU waste mixtures,
- establish safe TRU waste management approaches with respect to limiting environmental conditions,
- determine probable causes in event post mortem analyses.

In particular, our success emphasizes the value of using the ARC or equivalent to evaluate waste stabilities.

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Acknowledgements