

Analysis of the Reactivity of RadPro[®] Solution with Cotton Rags

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
under Contract DE-AC06-08RL14788



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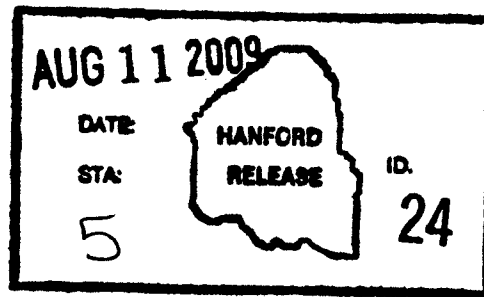
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LIST OF ACRONYMS

- ARC Accelerating Rate Calorimetry
- CCPS Center for Chemical Process Safety
- DTA Differential Thermal Analysis
- HF Hydrogen Fluoride
- MS Mass Spectrometry
- MSDS Material Safety Data Sheet
- PFP Plutonium Finishing Plant
- PNNL Pacific Northwest National Laboratory
- TGA Thermogravimetric Analysis

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1.0 BACKGROUND AND PURPOSE

Rags containing RadPro[®] solution will be generated during the decontamination of the Plutonium Finishing Plant (PFP). Under normal conditions, the rags will be neutralized with sodium carbonate prior to placing in the drums. The concern with RadPro solutions and cotton rags is that some of the RadPro solutions contain nitric acid. Under the right conditions, nitric acid and cotton rags exothermically react. The concern is, will RadPro solutions react with cotton rags exothermically?

The potential for a runaway reaction for any of the RadPro solutions used was studied in Section 5.2 of PNNL-15410, *Thermal Stability Studies of Candidate Decontamination Agents for Hanford's Plutonium Finishing Plant Plutonium-Contaminated Gloveboxes*. This report shows the thermal behavior of cotton rags having been saturated in one of the various neutralized and non-neutralized RadPro solutions. The thermal analysis was performed using thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Accelerating Rate Calorimetry (ARC).

The worst case reaction was found for the case of a cotton rag soaked in a solution of RadPro "A". RadPro "A" is comprised of 75% RadPro 0200 and 25% RadPro 0300. Using Table 5.4 of PNNL-15410, RadPro A, as of September 2005, is:

- Hydrochloric acid (HCl) 0.8% to 3.8%
- Ammonium fluoride (NH₄F) 1.5% to 3.8%
- Citric acid (C₆H₈O₇) 0.8% to 2.3%
- Nitric Acid (HNO₃) 1.3% to 6.3%
- Chemical buffers and agents

It should be noted that the current formulation (as of June 5, 2009) will have

- 0.8 % phosphoric acid (as compared to 0.8% to 3.8% hydrochloric acid)
- 0.8% ammonium bifluoride (as compared to 1.5% to 3.8% Ammonium fluoride)
- The same amount of citric acid
- 0.3% to 1.3% nitric acid (as compared to 1.3% to 6.3% nitric acid).

The current formulation is less able to start an exothermic reaction (see below). As a result, the 2005 version of the formulation of RadPro "A", studied in this paper, represents a bounding case.

The liquid soaked rag was dried in a flowing air stream at ambient temperature for 24 hours. The dried rag was placed into the ARC. The ARC was then started on its heat-wait-search mode. In this mode, the ARC heats the sample. There is a wait time in which the ARC is looking for evidence of self-heating.

If the self-heating rate is less than 0.01 C/min, the ARC heats to the next temperature "step" and heats again. If a self-heating reaction occurs, the ARC provides heating to itself to preserve the adiabatic nature of the calorimeter until the self-heating drops down to less than 0.01 °C/min

[®] RadPro is a registered trademark of Environmental Alternatives Incorporated, Keene, New Hampshire.

again. When this happens, the ARC, again, starts on the heat-wait-search mode from the last temperature attained.

A second sample, prepared in the same way, was placed into a Differential Thermal Analyzer/Thermalgravimetric Analyzer (DTA/TGA). The DTA measures the temperature difference between the sample and an inert reference material having about the same mass. The TGA measures mass loss.

For the cotton rag soaked in RadPro solution "A" and air dried for 24 hours at ambient temperatures, the DTA showed an 8 % weight loss and net heat loss (endothermic) between ambient and 125 °C.

Of particular interest is Figure 5.22 which shows the ARC plot (time rate-of-change of temperature vs. temperature) of a cotton rag that was saturated in RadPro decontamination solution "A", had been dried out, and then was then placed into the ARC analyzer. The figure appears to show an exothermic reaction starting at 70 °C (rate of change of temperature of 0.004 °C/min-g). At 100 °C, the heat rate peaks (at about 2 °C /min-g) and then decreases with little temperature change down to below 0.01 °C /min-g at 105 °C. A second exothermic reaction starts at about 109 °C and continues until about 200 °C, where it peaks at 2 °C /min-g. The curve again decreases to about 0.1 °C /min-g. The curve remains at or below 0.1 °C /min-g to 400 °C. The pressure at the end of the first spike (at about 100 °C) was less than 100 pounds per square inch (psi). That is, the pressure corresponding to the top of the thick line that represents pressure on Figure 5.22 is about 100 psi. It should be noted that the thickness of the line is about 80 psi. The middle of the thick line indicates a pressure of about 50 psi.

The question is the following: Is the first "spike" in the ARC a reaction curve of cotton and RadPro A? The PNNL report concluded that the ARC showed a self-propagating exothermal reaction starting at 70 °C. The PNNL report states:

The ARC, as shown in Figure 5.22, observed a self-propagating exothermic activity in the dried decontamination solution soaked cotton rag beginning at 70 °C ... The first reaction continues beyond 100 °C, but another exothermic reaction starts at 105 °C .

The question is the following: Is the first "spike" in the ARC curve of cotton and RadPro A indicative of a self-propagating exothermal reaction?

The report was reviewed by Ted Venetz, PFP Engineering. Section 3.0 was additionally reviewed by Dr. Scott Barney, retired PFP chemist.

2.0 CHARACTERIZING THE THERMAL BEHAVIOR OF UN-NEUTRALIZED RADPRO SOLUTION "A" ON COTTON RAGS AS EXOTHERMIC IS CONSERVATIVE

Exotherm and Endotherm at the same temperatures

The first indication that the exotherm might not be a propagating self-heating reaction at the specified onset temperature of 70 °C is the paragraph discussing the TGA/DTA analysis of the same type of rag and RadPro solution in Figure 5.21. Page 5.22 of PNNL-15410 states that:

Figure 5.21 shows an initial endothermic 8% mass loss occurring between ambient and 125°C likely due to residual water and possibly some of the two volatile acids.

Figure 5.21 shows decreasing heat flow between ambient temperatures and about 110 °C. The heat flow increases between 110 °C and about 300 °C, with a steep increase in heat flow from about 220 °C to 300 °C. Had the ARC curve indicated an exothermic reaction, the heat flow on the TGA/DTA curve would have been sloped upward in this region, not downward. It should also be noted that between ambient and 110 °C or so, absorbed water and possibly chemically absorbed water is evaporating. It takes energy to evaporate water in either a closed system (the ARC) or an open system (TGA/DTA). The self-heating propagating reaction would have to release more energy than required to evaporate water for an exotherm to show.

However, Section 4.3 of PNNL-15410 states that the differences in the ARC plot and the TGA/DTA plot are reasonable and imply that the differences do not indicate that no exothermal reaction occurred. The report states the following:

Two different instruments can produce apparently contradictory results because of their differing open and closed designs. In the TGA/DTA and TGA/mass spectrometry (MS) systems, the sample cell is open, gases produced through evaporation or reaction are removed with the sweep gas, and the system pressure remains constant. Loss of starting material may decrease the overall energy produced by sweeping away reactive gases. Because the ARC is a closed system, all gases produced stay in the sample cell unless the container fails. Vaporization is suppressed by the increased pressure in the reaction vessel. Dissociative reactions that are endothermic and vapor pressure dependent are suppressed. Consequently, self-heating reactions may be observed at lower temperatures than for open systems. Studies have found differences in ammonium nitrate behavior in open and closed systems. In open systems, ammonium nitrate vaporization can occur easily, and significant loss of the starting material can occur, preventing a well-known self-propagating reaction. They also report that onset temperatures for vented systems are lower than for closed systems, but the times to runaway are also longer, in general.

Reaction does not look like a classic self-propagating exothermic reaction

The second indication is that the curve in Figure 5.22 is not typical of a self-propagating reaction. The ARC curves for material exhibiting these reactions usually show an increasing rate-of-change of temperature vs. temperature plot until a peak is reached. After the peak, the rate-of-change of temperature rapidly decreases. Soon after the decrease starts, the curve stops as the reacting material has been used up. The curve never goes up again, as that in Figure 5.21 does. Self-propagating exothermic reactions do not, typically, start, stop and then start again unless there are two separate reactions going on and they are separated such that heat has to be externally applied to get to the onset temperature of the second reaction. This is not likely the case with RadPro "A" and cotton rags.

Results from ARC using rags are not reproducible

The third indication that the curve in Figure 5.22 might not signify an exothermic reaction is to consider the ARC curves shown in Figure 5.23. Figure 5.23 provides the self-heat rate and pressure as a function of temperature for two runs of sodium hydroxide neutralized cotton rags that once contained RadPro solution "A". The PNNL report states the following with regards to this curve:

We used the ARC to investigate the thermal reactivity of the hydroxide-neutralized RadPro decontamination solution (RadPro A). As shown in Figure 5.23, in our first analysis (3-day old material) the ARC found that neutralization with sodium hydroxide delayed the onset temperature (for the self-heating reaction) from 70°C (as observed for RadPro A alone) to 170°C (with neutralized RadPro A). (That is, there was only one peak which started at 170 C.) The second ARC analysis (9-day old material) found some exothermicity at 45°C but the reaction was not self-heating. A second reaction began at 115°C and sustained itself to 150°C where a third self-sustaining reaction began and lasted to 280°C where a fourth reaction began and continued to the end of the experiment. The significant differences between the two analyses cannot be easily explained because there was only 6 days between the two analyses and they were performed using the same ARC.

The point is that essentially the same material (3-day vs. 9-day material) run with the same ARC gave significantly different results (a self-heating initiation temperature of 170 °C vs. either 45 °C or 115 °C initiation temperature with further differences in the curves at greater temperatures).

PNNL uses the Center for Chemical Process Safety (CCPS) "rule-of-thumb" difference of a 50 °C between what the ARC analysis observes as the onset temperature for self-heating temperature and "reality". It is interesting to note that the onset temperature for these two runs is 65 °C (170 °C vs. 115 °C). It is therefore possible that the onset temperature for cotton rags in Rad Pro Solution "A" is 120 °C, not 70 °C. That is, the 70 °C case could have been indicative of a propagating reaction occurring at 120 °C, but in this case, initiated at 70 °C rather than 120 °C.

Manufacturer does not believe there is any exothermic activity

The fourth indication that the data found from Figure 5.22 is suspect is the following e-mail received from Randy Martin, Vice President, Environmental Alternatives, Inc. Mr. Martin writes:

We have been using this product very successfully and very safely for 10 years or so and work has been done at many DOE sites as well as commercial nuclear facilities. There has never been any issue with reaction occurring with any of the waste generated by our process in the long history of its use. The previous work that we did at sites other than Hanford did not even incorporate the sodium carbonate neutralization step that has been used at Hanford.

Our chemistry is designed to be used in ratio blends and all acids used in our formulas are highly buffered. The formulations are designed to react with each other and the substrate during the application process and completely react out to leave behind water, CO₂ and some trace harmless salts. The application and removal process also requires a DI water rinse as part of the step prior to being removed with the rags. All of these factors are designed to react out and neutralize the final waste product rendering it safe for disposal. Hanford has added an additional step that requires the rags to be neutralized further with sodium carbonate and then checked with a pH strip prior to bagging the waste out of the glovebox.

The data from the PNNL report does show some exothermic peaks at certain temperatures but our belief is that the waste form of our product is no more reactive than just the straight cotton rag would be at those temperatures.

ASTM Standard provides discussion of potential problems in using ARC for solid and/or heterogeneous materials

The fifth indication is the following. The first peak in Figure 5.22, which PNNL stated was an indication of a self-propagating exothermic reaction could be a failure of the ARC to properly measure the conditions in the sample holder. Section 6.1 of ASTM Standard E 1981-98, *Standard Guide for Assessing Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry*, states that use of accelerating rate calorimetry requires good heat transfer within the sample and between the sample and the sample holder and is therefore subject to the following limitation:

- Solid Samples may not yield quantitatively reliable or consistent results
- Heterogeneous systems may not give meaningful results
- Other limitations that do not pertain to the analysis of cotton in RadPro "A"

The fact that the cotton rag with dried RadPro decontamination solution "A" on it is a solid heterogeneous sample might be the reason why the temperature spike is seen.

Conclusion

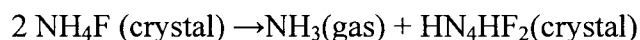
All of the above point to the conclusion that while PNNL believes that they found evidence of exothermic activity, there is also evidence that either none exists or that what they found actually occurs at higher temperatures.

3.0 IS IT POSSIBLE THAT AN EXOTHERMIC REACTION COULD OCCUR?

A reasonable interpretation is that the ARC curve must be compatible with the response seen on the same material in the TGA/DTA curve. It is clear that water is present in the material and must first be evaporated before a reaction can occur. This is seen effectively in the TGA/DTA with a very slight weight loss, and endotherm continuing to about 130 °C (must be free water and some harder to evaporate material captured in the cellulose molecule). At the same temperature the ARC data shows a self-heating spike (exotherm) peaking about 100 °C. It cannot be both at the same time. The DTA is more believable because water must be evaporated and that process is endothermic. It is also noted that the self heating stops and drops to background (not a runaway). Physically what might be happening is that as the water evaporates, the relative humidity in the sealed bomb goes way up. This increases the thermal conductivity of the bomb/sample. This change in thermal conductivity could be interpreted as an exothermic reaction, when it is merely an increase in the thermal efficiency of the ARC heater/thermocouple response.

On the other hand, the exothermic reaction, starting at 70 °C may be real. It might be that the constituents of the RadPro solution react with the cotton rag at elevated temperatures or that the constituents decompose into a chemical that reacts with cotton rags.

The journal article *The Properties and Reactions of Ammonium Fluorides* states that when heated, ammonium fluoride decomposes in the following way:



The reference provides an equation for the equilibrium pressure of the gaseous products that starts at 343 K (70 °C). The equation for equilibrium pressure for temperatures between 343 K and 383 K (110 °C) is:

$$\text{Log } P(\text{mmHg}) = -8.82996 - \frac{3022.966}{T} + 6.87415 * \text{Log } T$$

The equation for equilibrium pressure between 404 K and 439 K is:

$$\text{Log } P(\text{mmHg}) = 47.863 - \frac{6582}{T} - 11.365 * \text{Log } T$$

The results are as follows:

Equilibrium Pressure for the gases from the decomposition of Ammonium Fluoride

Temp, K	333 (extrapolated)	343	373	404	411	440
Log P	-0.56828	-0.21528	0.743886	1.949397	2.142089	2.861069
P, mmHg	0.270224	0.609144	5.544799	89.00135	138.7041	726.222

Various Material Safety Data Sheets (MSDS) for Ammonium Fluoride show that:

“Emits toxic fumes of hydrogen fluoride, nitric oxides and ammonia when heated to decomposition” (Section 10 of the MSDS – Stability and Reactivity).

Lastly the textbook *Handbook of Inorganic Chemicals*, states the following:

“Ammonium fluoride decomposes on heating to ammonia and hydrogen fluoride and decomposes in hot water producing ammonia and ammonia bifluoride (NH₄HF₂)”.

The above shows that the ammonium fluoride, since it is not in hot water, can decompose into ammonia and hydrogen fluoride (HF). If the MSDS is correct, nitric oxides might be present as well.

Recent formulations of RadPro solution “A” contain Ammonium bifluoride. A review of the same three references show that the products of decomposition are the same (*Handbook of Inorganic Chemicals* additionally states that at high temperatures, decomposition yields ammonium and hydrogen fluoride [HF]). The Russian Journal provides an equation for the equilibrium pressure of the gas from ammonium bifluoride. The start of gas evolution is 343 K (70 °C) (like ammonium fluoride). However, solving the equation shows that the amount of gas is less (pressure is less at the same temperature).

The equation for equilibrium pressure for temperatures between 209 K and 399 K is:

$$\text{Log } P(\text{mmHg}) = -6.723 - \frac{3295}{T} + (6.915 * \text{Log } T) - (0.00547 * T)$$

The equation for equilibrium pressure between 392.5 K and 412 K is:

$$\text{Log } P(\text{mmHg}) = 20.809 - \frac{4256}{T} - (3.6 * \text{Log } T) - (0.00028 * T)$$

The results are as follows:

Equilibrium Pressure for the gases from the decomposition of Ammonium BiFluoride

Temp, K	333	343	383	399	411
Log P	-0.9967	-0.67407	0.441676	0.667111	0.928858
P, mmHg	0.100762	0.211804	2.76488	4.646339	8.489034

Since ammonium fluoride was used in the PNNL study, it will be used in this paper as well. It should be noted that the above partial pressures are well below that seen in the ARC analysis. Simple decomposition does not cause the pressurization.

RadPro "A" also contains hydrochloric acid and nitric acid. Could the acids have started the reaction?

A Google search of the Internet for hydrolysis reactions of cellulose with acids showed a patent application (www.freepatentsonline.com/4637835.html) in which cellulose, water, a CaCl_2 catalyst and HCl (which is a component of the RadPro solution "A" tested by PNNL) is used to hydrolyze cellulose. The reaction is said to be exothermic. The article also states that hydrolysis is performed at 175 °C, that is, the reaction occurred at 175 °C. The pressure needed to be at least 160 psig for the reaction to proceed exothermically. It should be noted that only the old formulation of RadPro "A" uses hydrochloric acid (HCl), the present formulation does not use HCl, it uses phosphoric acid. The reactions discussed in this paragraph do not occur with phosphoric acid.

A presentation found on the Internet (<http://www.registratieplatform.nl/UserFiles/File/Nijman.pdf>) by N2 Ethanol Hardenberg BV states that weak acid hydrolysis of cellulose is exothermic. A related presentation shows that the hydrolysis occurs at around 200 °C. Weak acid hydrolysis, as described above, could not have started the reaction seen at 70 °C and the initiation temperatures are much greater.

RadPro solution "A" contains ammonium fluoride. This decomposes, on heating, into HF. Could the HF cause the reaction?

The chemical HF does react with cellulose exothermically at low temperatures. This reaction is described in United States Patent 4,556,432 (Dec 3, 1985), *Process for Hydrolyzing Cellulose-Containing Material with Gaseous Hydrogen Fluoride*. The patent describes a process in which granulated lignocellulose (obtained as the residue from a preliminary hydrolysis of spruce wood) was conveyed into a sorption reactor. HF-Nitrogen mixtures at different concentrations flowed into the reactor to react with lignocelluloses. The reactor contained 60 grams HF to 100 g lignocelluloses. The conditions were 50 °C. No specific reaction pressure was provided, however, the introduction to the process discussed similar processes conducted at atmospheric pressure. The resulting reaction was exothermic.

While the temperature in the case of the RadPro "A" is a little greater, the

- Rag is not granulated,
- Has not been previously hydrolyzed, and
- The ratio of HF to cellulosic material in the process described in the Patent is 60:100. The ratio of HF to cotton rag is much less. This is shown by the following. At 100 °C,

the partial pressure of gases from decomposition of ammonium fluoride is 5.5 mmHg or 7.2×10^{-3} atm (See partial pressure of gaseous components from the decomposition of ammonium fluoride, above). The Russian Chemical journal states that the decomposition produces ammonia. Assume that the journal is not correct and that the *Handbook of Inorganic Chemicals*, which states that the decomposition produces ammonia and hydrogen fluoride (HF). Further assume that all of the decomposition product is HF (no ammonia is formed). Lastly, assume that the partial pressure of HF is that given for ammonia in the Russian chemical journal. Using the ideal gas law with the above pressure, free volume in the ARC sample holder of 8.5 ml [See Section 3, below] and a temperature of 100 °C shows that the number of moles of HF present is 2.0×10^{-6} or 4×10^{-5} g of HF). The ratio of HF to cotton rag is 4×10^{-5} to 2, not 60 to 100.

It is not likely that the HF could be the cause of the exothermic reaction as there is little HF present as compared to mass of the cotton rag and the rag has not been previously hydrolyzed or granulated.

The MSDS stated that NO_2 is a product of the decomposition. The NO_2 comes from the ammonia in ammonium fluoride. It might also come from the dried nitric acid on the rag.

The journal article *Thermoanalytical Studies on the Durable-Press Curing of Cellulose, Part II: The Effect of Nitrate Salts on the Thermal Behavior of Cotton* discusses reactions of cotton with zinc nitrate. Cotton treated with solutions of zinc nitrate show weight loss, along with “large evolutions of heat”. The document states that, on heating, zinc nitrate decomposes into zinc oxide and nitrogen dioxide. The document then theorizes that the nitrogen dioxide (NO_2), a strong oxidizing agent, degrades the cellulose creating heat (exothermic degeneration). Since one of the decomposition products of ammonium fluoride could be NO_2 , and since the reaction of NO_2 with cotton is exothermic, the release of NO_2 during decomposition could be the cause of the exothermic reaction seen in the ARC. It should be noted that zinc nitrate melts at 36 °C. Nitrate salts are more reactive when molten. Nitrate salts could also decompose at temperatures near the melting point and react with cellulose. The nitrate salts from the RadPro solution is much more stable.

If NO_2 is a product of decomposition of ammonium fluoride or if it arises from heating the dried nitric acid, there is likely to be little NO_2 present (See HF calculation above). Therefore, the presence of NO_2 is not likely to be the cause of the exothermic reaction at 70 °C.

Conclusion

The above suggests that an exothermic reaction will likely not start within the RadPro soaked rag at about 343 K (70 °C), the temperature at which gases from the decomposition of ammonium fluoride appear as:

- the constituents of RadPro “A” (the acids) do not appear to react at those conditions;
- the decomposition constituent (HF, NO₂) concentration is too small;
- one of the potential constituents (NO₂) may not even be an actual constituent.

Therefore, it is unlikely that the first spike in the temperature vs. heat rate curve in the ARC analysis of RadPro “A” is “real” (an indication of exothermic activity).

4.0 POTENTIAL IMPACTS ASSUMING THAT THE EXOTHERMIC SPIKE IS REAL

For purposes of further discussion, it will be assumed that the first spike is real in the ARC analysis of RadPro “A” with cotton rags, even though there is every indication that it is not. Given that the reaction occurs, what does this mean for the waste drum.

Figure 5.22 of PNNL-15410 shows that at 100 °C, the pressure in the sample holder had increased to about 50 psig (4.4 atm). The PNNL report states that the volume of the sample holder is 10 ml. the mass of the sample is “<3 g” per the report. It is assumed that the sample weighs 2 g. The density of a single cotton sheet is 86.4 lb/ft³ or 1.38 g/cm³ per the *Plastic Material Data Sheets*. The bulk density of tightly packed cotton or cotton wool is 0.08 g/cm³ or 5 lb/ft³ per page 312 of the *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, and 9 lb/ft³ per PFP measurements. The free volume in the sample holder is then 8.5 ml. At the initial conditions when the sample is sealed (atmospheric pressure and an assumed 298 K [25 °C]), there are 0.00035 moles of air in the sample.

As the sample heats up, water vapor also comes out. Figure 5-8 of the *Cotton Ginners Handbook* provides the moisture content of cotton fiber. At a relative humidity of 40%, typical for indoors, at 70 F, Figure 5-8 shows that the moisture content is 6%. This means that a 2 g rag would have 0.12 g of water or 0.0067 moles. Assume that all of the water came out of the rag as water vapor between ambient and 100 °C. This would result in a pressure within the sample holder of 25 atm or 356 psig. If the moisture content was 1/10 of this (0.6%) the pressure would be 3.6 atm or 39 psig. The evolution of water vapor from the drying rag could be the cause of the entire pressure increase seen in the sample holder.

The ideal gas law is used to determine the number of moles of gas in the sample holder after the reaction to 100 °C. It is conservatively assumed that the pressure in the sample holder is 100 psig or 7.8 atm. The moles of water vapor present is conservatively based on a moisture content of 1.2%, five times less than that at normal room conditions. The total moles of air and water vapor in the sample holder at 100 °C is 1.7×10^{-3} moles (based on 0.00035 moles of air and 0.00133 moles of water vapor).

At 7.8 atm and 100 °C, the number of moles in the sample holder is 2.2×10^{-3} moles. Therefore, 2 g of cotton rag reacts at 100 °C to form 0.0005 moles of gas (from 0.0022 moles total gas minus 0.00035 moles of air and 0.00133 moles of water vapor).

Now consider a drum having a volume of 208 L. Assume that the bulk density of cotton rags is twice the bulk density of cotton or cotton wool or 0.16 g/cm^3 or 10 lb/ft^3 , a value similar to that found at PFP. Within this drum, one could put 33 kg of rags. If 2 g of cotton rag creates 0.0005 moles of off-gas and 0.00035 moles of water vapor, then 33 kg of cotton rags, all heated to 100 °C and all reacting like Figure 5.22 of PNNL-15410, would release 14 moles of gas. The actual volume taken up by the 33 kg of cotton rags is 24 L based on a cloth density of 1.38 g/cm^3 . Initially, the drum contains 7.5 moles of air based on a pressure of 1 atm, temperature of 25 C (298 K) and volume of 184 L. The final pressure in the drum, at 100 °C based on the 7.5 moles of air initially present and the 14 moles of off-gas and water vapor evolved from heating the cotton is 3.6 atm or 38 psig based on a final temperature of 100 °C (373 K), 184 L volume and 21.5 moles of gas. Loading the drums with a greater quantity of rags would result in a greater pressure as more gaseous products would be released into a smaller free volume. Loading the drums with a lesser quantity of rags would result in a lower pressure as the gases would be released into a larger free volume.

However, not all of the rags get to 100 °C. Consider a green waste drum loaded with cotton rags that had been soaked in RadPro solution “A” and dried, but not neutralized. Assume that the drum is located in the hot sun. Assume that after an evening of cooling, the drum contents are at 109 °F (37.8 °C). Then assume that the next day, the external shell of the drum is heated instantly to 210 °F. The condition is a cylindrical volume having heat applied via radiation and conduction due to hot walls. This problem requires a computer solution. To get a feel for the conditions inside the drum and to make the calculation simpler, the condition is modeled as a semi-infinite slab with a sudden increased temperature at the surface. The equation for the temperatures comes from Section 2.5 of *Conduction of Heat in Solids*. The equation is for a semi-infinite slab having an initial temperature of 0 °F and a temperature of T_o suddenly applied to the edge of the slab. The equation is:

$$T(x, t) = T_o * \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha t}}\right)$$

Where

T_o = Temperature applied to surface of slab = 210 °F

x = distance into the slab, cm

α = thermal diffusivity of cotton, cm^2/s
= $0.0063 \text{ cm}^2/\text{s}$

t = time after increased temperature was applied, s

In this case, since the initial temperature is not 0 °F, the equation is:

$$\frac{T(x, t) - T_i}{T_o - T_i} = \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha t}}\right)$$

Substituting the values used for the initial temperature and the suddenly applied wall temperature yields:

$$T(x, t) = 109 + \left[(210 - 109) * \operatorname{erfc} \left(\frac{x}{2\sqrt{\alpha t}} \right) \right]$$

The equation was put into an EXCEL spreadsheet. The results are shown in Table 1.

Table 1 – Temperature of Waste in Heated Drums

Time after increased temperature was applied, s	3600 (1 hour)	7200 (2 hours)	10800 (3 hours)	18000 (5 hours)	28800 (8 hours)	43200 (12 hours)
Value of “ αt ”	22.68	45.36	68.04	113.4	181.44	272.16
Distance from surface of slab, cm	Temperatures at the time above and the distance from the surface of the slab (see left), F					
1	198.0785	201.5547	203.10026	204.6529	205.7716 (96.5C)	206.547 (97 C)
3	175.2565	185.0312	189.50163	194.0524	197.3611 (91.9C)	199.6662 (93 C)
6	146.6728	162.4021	170.30813	178.7232	185.0312 (85 C)	189.5016 (87.5 C)
10	122.8977	138.6701	148.52249	160.1747	169.5614 (76.4 C)	176.4881 (80 C)
13	114.4115	126.4016	135.77532	148.1896	158.9913 (70.6 C)	167.316 (75 C)
29	109.0017	109.2352	110.3048	114.469	121.9199 (50 C)	130.6007 (54.8 C)

This data compares well with the PNNL temperature data shown in Figures 3 and 4 of the letter report *Transmittal of Rag Barrel Heat Transfer Analysis* for green drums.

In the PNNL thermal analysis report, a green surface drum with 4 Watts being generated in the center 8 inches of the drum has a peak surface temperature of 213 °F and peak waste temperature of 206 °F (97 °C). The analysis above shows a peak temperature of 206.5 °F for waste 1-cm from the edge. Figures 3 and 4 of the PNNL thermal analysis show the vertical temperature distribution in two regions of the drum at 1 pm (9 hours into the heating cycle). While not specifically stated within the report, it is assumed that these two figures represent the point in time and location within the drum where the effects of heating are most pronounced. Figure 3 and 4 of the PNNL thermal analysis show that the waste that is at high temperatures (>150 °F) comprise only about 20% of the total waste. The analysis above shows about 1/3 of the waste has high temperature (> 87 °C or 189 °F). The analysis performed above is more conservative than the PNNL Thermal study.

The point is that even under extreme heating, only a part of the rags get hot enough to react exothermically. In this case, the main reaction occurs only in the first 5 cm of the slab (at 90 °C, the self-heat rate from Figure 5.22 is about half of that at 100 °C). The rest hardly reacts at all. Assume that these distances apply to a waste drum. Assume that from the outer edge to 5 cm in reacts at the rate of 2 C-min-g (such that 50 psig of gases is evolved). Given that the radius of the drum is 11.25 inches or 28.6 cm. The fraction of the drum volume that reacts is about 1/3.

Applying the 1/3 factor to the 14 moles of gas that evolved assuming all of the waste reacted, yields 4.7 moles reactants and water vapor. The final pressure is 1.9 atm or 13 psig based on a free volume of 184 L, final temperature of 70 °C (approximate average in the drum) and total moles of 12.2. It should be noted that the heat evolved from the 1/3 of the drums reacting may be sufficient to heat the other drums to the point where they react and give off heat. However, there will also be heat transfer out of the drum during the time that the heat from the drums which reacted heats those which were assumed not to react. As a result, the pressure may be somewhat greater than 13 psig, but likely less than 38 psig.

The 55-gallon drums are open head drums. DOE-STD-5506-2007, appendix B, Section B.2.6 provides the results of tests on drums in which the pressure was slowly (as compared to deflagrations) increased within the drum. This would be the case should the first self-heating Spike be real and the temperature get to the point where that reaction can occur. The results for open-headed drums are:

- Drums appear to vent immediately adjacent to nut and bolt fastener on ring, causing a crease in the metal at that location.
- Pinging was noticeable between 15 and 20 psig.
- 100% of the drums tested vented at pressures at or below 32 psig.
- The 55-gallon metal open-head drums appear to bulge at only top and bottom ends.
- Body seam (top and bottom) experienced no visible distortion or apparent weakening.

Conclusion

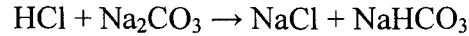
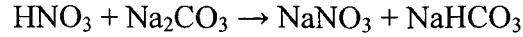
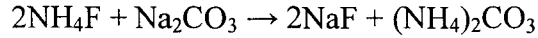
The green drums can withstand the resulting pressure, should the first spike on Figure 5.22 actually occur, and assuming that all (100%) of the rags in the drum react at the same time as the pressure, for this case is 38 psig. For the more realistic case where only 1/3 of the rags react (because only 1/3 of the rags get to temperatures that are great enough for a significant reaction to occur; the rest are at much lower temperatures), the pressure is between 13 psig and 38 psig. The drums can withstand this pressure.

If the PNNL thermal analysis is revised, it would be of benefit to have figures for the worst case drum showing vertical and radial temperature distributions in various locations to show more clearly the effects of heating the waste.

5.0 RESULTS OF TESTING THE OTHER RADPRO SOLUTIONS

Table 2 below provides the results of testing other RadPro solutions.

For the cases in which the solution is neutralized with sodium carbonate, the constituents are:



There is no acid left for acid hydrolysis. Hydrogen Fluoride will not be a constituent as the HF producing chemical is transformed. There is no NO_2 as the decomposition temperature of NaNO_3 is 380 C and the products are sodium oxide and oxygen with the potential for NO at even greater temperatures. As a result, one would expect no exothermic reactions until the cotton itself, exothermically reacted, as there are no chemical species that might cause a lower temperature reaction.

Table 2 – Results of the all of the Cases in the PNNL study

PNNL-15410 Section (Figure number showing ARC data)	RadPro solution	cloth	Neutralized?	Temperature (°C) at which there is the first onset of self-propagating exothermic per the PNNL-15410 authors)
5.2.1 (Figure 5.22)	“A”	Cotton	None	70
5.2.2.1 (Figure 5.23)	“A”	Cotton	Neutralized in Sodium Hydroxide	115 (second reaction starts around 150 °C) and 170 for the 9-day and 3-day old material, respectively
5.2.2.2 (Figure 5.24)	“A”	Cotton	Neutralized in Sodium Carbonate	120 (second reaction starts at about 160 °C)
5.2.3	RadPro “B” (33% Decon and 67% Rinsate)	Cotton	None	130 (obtained with DTA - (100 °F uncertainty – very small spike, about 0.25 mV/g at 130 °C vs. 1.8 mV/g spike starting at about 220 °C)

5.2.3 (Figure 5.27)	RadPro "B" (33% Decon and 67% Rinsate), then the cotton cloth was used to wash stainless steel.	cotton	None	90 The ARC curve that shows a reaction at 90 °C are only portions of, what should be, a complete curve on a graph.. There is no run-up temperature data. The curve essentially starts at the peak without any indication of how it got to that temperature and the decrease in self-heating rate past the peak. It would be helpful if the analysis were re-done so that a complete curve of self-heating vs. temperature from 50 °C to 450 °C could be studied
5.2.4	"C"	Cotton	None	250
5.2.5	"D"	Cotton	None	None
5.2.6	"E"	cotton	None	None
5.2.7 (Figure 5.31)	RadPro 0200 and 0300 and RadPro 0100 with Rinsate	Cotton	Neutralized	Two short lived reactions: one at 70 and one at 90 (second large peak starting at around 150 °C) However, the figure (Figure 5.31) shows 2 data points, only, that supposedly defines these peaks. No steady run-up in self heat rate, no indication of onset temperature, no decrease in self-heat rate It would be helpful if the analysis were re-done so that a complete curve of self-heating vs. temperature from 50 °C to 450 °C could be studied

5.2.8.1 (Figure 5.32)	"A"	20% Polyamide and 80% Polyester	None	80
5.2.8.2 (Figure 5.33)	"A"	20% Polyamide and 80% Polyester	None	135 (4-day old material) 95 (304-day old material) The self-heating rate for the 304 day old material is essentially flat at 1E-2 C/min-g. The self heating rates for the 4-day old material consists of 3 data points. It would be helpful if the analysis were re-done so that a complete curve of self- heating vs. temperature from 50 °C to 450 °C could be studied
5.2.8.3	"A"	50% Polyamide and 50% Polyester	None	115
5.2.8.4	"B"	50% Polyamide and 50% Polyester	None	156
5.2.8.5 (Figure 5.38)	"C"	50% Polyamide and 50% Polyester	None	80 for 5-day old material
5.2.8.6	RadPro 0100	50% Polyamide and 50% Polyester	None	320
5.2.8.7	"E"	50% Polyamide and 50% Polyester	None	290

Solution Identification		Solution Composition, vol%		Description	
RadPro A		75% RadPro 0200/25% RadPro 0300		Decontamination Solution	
RadPro B		33% RadPro A - 67% RadPro C		Decontamination + Rinsate	
RadPro C		10% RadPro 0300/90% DIW		Rinsate	
RadPro D		RadPro 0100		Emulsifying Solution	
RadPro E		67% RadPro C - 33% RadPro D		Emulsifier + Rinsate	
RadPro 0100		RadPro 0200		RadPro 0300	
<u>Ingredient</u>	<u>Concentration</u>	<u>Ingredient</u>	<u>Concentration,</u>	<u>Ingredient</u>	<u>Concentration,</u>
Ethylene glycol monobutyl ether	5-15%	Hydrochloric acid	1-5%	Nitric Acid	5-25%
Triethylamine	0-1%	Ammonium fluoride	2-5%	Chemical Buffering Agents and water	???
Isopropanol	0-2%	Citric acid	1-3%		
Potassium hydroxide	1-5%				

The only cases where there is a low temperature self-sustaining reaction is in

- Section 5.2.1 – RadPro A – 70 °C – Peak self-heating rate for first spike is 2 °C/min-g (nitric acid, ammonium fluoride, hydrochloric acid)
- Section 5.2.3 – RadPro B – 90 °C - Peak self-heating rate for first spike is 0.5 °C/min-g (nitric acid, ammonium fluoride, hydrochloric acid)
- Section 5.2.7 – RadPro 001, 002 and 003) – 70 °C - Peak self-heating rate for first spike is 0.5 °C/min-g (nitric acid, ammonium fluoride, hydrochloric acid)
- Section 5.2.8. 5 – RadPro C –70 °C - Peak self-heating rate for first spike is 1.0 °C/min-g (nitric acid)

The constituents for these all of the reactions are the same as that for RadPro “A” discussed in Section 3. The conclusions regarding whether or not the spike is real is the same; it is very likely not.

5.0 CONCLUSION

RadPro is safe to use, even without neutralization, for the following reasons:

- The PNNL study appeared to find 4 cases where the onset temperature for self-heating exothermic reactions are within 50 °C of Hanford's peak temperature (45 °C). This would indicate that a self-heating propagating reaction could occur within the waste due to heating from the sun and ambient temperature, consistent with an ambient temperature of 45 °C (113 °F). However, there is evidence to suggest that the PNNL data is not indicative of a self-heating propagating reaction. The evidence is:
 - Endotherm and exotherms at the same temperatures
 - The graph of the self-heating exothermic reaction (or runaway reaction) does not resemble a self-heating reaction because the rate of self-heating reaches a peak, drops to a very low value and then increases again. Typical reactions only stop when one or more of the reactants is exhausted.
 - The results from ARC are not reproducible
 - ASTM guidance for performing ARC cautions against using solid materials as the results can be unreliable and inconsistent.
- A review of the potential reactants that might cause an exothermic reaction found that:
 - they either do not occur (NO₂)
 - or they do appear and can react, but at higher temperatures, or
 - they do occur and can react with cotton, but the quantity present is so small that if they were capable of causing a self-heating reaction, it would be very weak and of short duration.

As a result, there is no apparent reason for the self-sustaining reaction.

- Even if the reaction occurs as indicated by the first spike in the ARC analysis of RadPro solution "A", a conservative analysis shows that the green drum is pressurized, but not beyond the point where the lid will blow out. This conclusion is only valid for reactions occurring between 70 °C and 100 °C. This is even more true for white drums, as the temperatures and resulting pressurization is less.
- The onset temperature for neutralized rags is 115 °C or 239 °F (ignoring the data in section 5.2.7 as it is difficult to interpret). This temperature exceeds the peak waste temperature for the worst case atmospheric heating event.

If the PNNL thermal analysis is revised, it would be of benefit to have figures for the worst case drum showing vertical and radial temperature distributions in various locations to show more clearly the effects of heating the waste.

It would be helpful if the analysis shown in PNNL 15410, Sections 5.2.3, 5.2.7, and 5.2.8.2 were re-done so that a complete curve of self-heating vs. temperature from 50 °C to 450 °C could be studied.

6.0 REFERENCES

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