THE USE OF A TREATABLILITY STUDY TO INVESTIGATE THE POTENTIAL FOR SELF-HEATING AND EXOTHERMIC REACTIONS IN DECONTAMINATION MATERIALS AT THE PLUTONIUM FINISHING PLANT

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ABSTRACT

Cerium Nitrate has been proposed for use in the decontamination of plutonium contaminated equipment at the Plutonium Finishing Plant located on the Hanford Nuclear Reservation in eastern Washington. A Treatability Study was conducted to determine the validity of this decontamination technology in terms of meeting its performance goals and to understand the hazards associated with the use of Cerium Nitrate under the conditions found at the PFP.

Fluor Hanford is beginning the decommissioning of the Plutonium Finishing Plant (PFP) at the Hanford site. Aggressive chemicals are commonly used to remove transuranic contaminants from process equipment to allow disposal as low level waste. Chemicals being considered for decontamination of gloveboxes in PFP include cerium (IV) nitrate in a nitric acid solution, and proprietary commercial solutions that include acids, degreasers, and sequestering agents. Fluor's decontamination procedure involves application of the chemicals, followed by a wipe-down of the contaminated surfaces with rags. This process effectively transfers the decontamination liquids containing the transuranic materials to the rags, which can then be readily packaged for disposal as TRU waste. As part of a treatability study, Fluor Hanford and the Pacific Northwest National Laboratory (PNNL) have evaluated the potential for self-heating and exothermic reactions in the residual decontamination materials and the waste packages. Laboratory analyses and thermal-hydraulic modeling reveal a significant self-heating risk for cerium nitrate solutions when used with cotton rags. Exothermic reactions that release significant heat and off-gas have been discovered for cerium nitrate at higher temperatures. From these studies, limiting conditions have been defined to assure safe operations and waste packaging.

INTRODUCTION

Fluor Hanford is beginning the decommissioning of the Plutonium Finishing Plant (PFP) at the Hanford site. Aggressive chemicals are commonly used to remove transuranic contaminants from process equipment to allow disposal as low level waste. Chemicals being considered for decontamination of gloveboxes in PFP include cerium(IV) nitrate in a nitric acid solution, and proprietary commercial solutions that include acids, degreasers, and sequestering agents. Fluor’s decontamination procedure involves application of chemical solutions as a spray on the contaminated surfaces, followed by a wipe-down with rags. This process effectively transfers the transuranic materials to the decontamination liquids, which are then absorbed by rags and packaged for disposal as TRU waste.

Concerns regarding the safety of this procedure developed following a fire at Rocky Flats in 2003. The fire occurred in a glovebox that had been treated with cerium nitrate, which is one of the decontamination chemicals that Fluor Hanford has proposed to use. The investigation of the event was hampered by the copious use of chemicals and water to extinguish the fire, and was not conclusive regarding the cause. However, the reviewers noted that rags were found in the glovebox, suggesting that the combination of rags and chemicals may have contributed to the fire. With that uncertainty, Fluor began an investigation into the potential for fire when using the chemicals and materials in the decontamination process. The focus of this work has been to develop a disposal strategy that will provide a chemically stable waste form at expected Hanford temperatures.

Treatability Tests

Treatability studies are conducted to assist in developing and executing remedial/removal actions under the CERCLA[1]. They provide site specific and condition specific information which assists in the evaluation of alternatives and the selection of remedies. Treatability studies also are used to determine if a specific remedy will work at the site and under the conditions necessary. Therefore it is important to conduct the treatability studies early in the process. Generally treatability studies identify performance goals, are conducted according to a design, use samples from the media of concern and report the results in a logical and consistent format.

Treatability studies are performed in the laboratory or in the field to obtain qualitative or quantitative data regarding the application of a specific chemical on specific wastes at site. Consequently a treatability study was determined to be important in determining the effectiveness and safety of using Cerium Nitrate at PFP to decontaminate equipment (gloveboxes) by removing plutonium from the surfaces of the equipment in order to dispose of the equipment as low level waste thus reducing the amount of TRU waste generated in the clean up process.

This study was performed to determine the implementability of the process and determine the safety of its use in the field. There was a concern that using the Cerium Nitrate at PFP could result in self-generation of heat and possibly result in a fire during the removal process. In this case a treatability study was needed to determine performance information with regard to waste types, types of wipes to be used and to determine if a neutralization was prudent and would be effective to prevent possible thermal reactivity.

As many as three [illegible]s of treatability testing may be performed: laboratory screening, bench-scale testing and pilot scale testing. Laboratory screening is used to determine if the technology is valid for the site's application. Bench scale testing is used to determine the technology's performance, and pilot scale testing is intended to provide information as to how effective the use of the technology is under field conditions.

This thermal reactivity treatability study was performed in the laboratory as a bench-scale test.

Proposed Decontamination Methods

Glovebox decontamination procedures are tailored for the specific chemicals used, but each of them have the following basic steps:

- A solution (or sequence of solutions) is applied to the contaminated surface, generally by spraying
- A dwell or contact time may be allowed for desired chemical or physical changes which transfer the contamination into the solution
- Residual solutions are removed, generally by absorption on towels or rags
- The contaminated towels or rags are packaged in plastic bags and sealed out into waste drums

Cerium Nitrate Decontamination Process

The cerium nitrate decontamination method involves spraying a solution of 0.25 molar cerci nitrate in 1 molar nitric acid onto the walls of a glovebox, allowing it react, then wiping off the solution. This dissolves any surface-deposited plutonium and chemically removes a thin layer of the metal surface along with any trapped plutonium. The rags used in for the removal of the decontamination solution are towels typically made of 86% cotton with 14% polyester.

Once a rag is mostly damp from soaking up the decontamination solution, it is treated with a 0.3 molar ferrous sulfate solution to reduce the ceric ion (Ce^{+4}) to cerous ion (Ce^{+3}). At this point, the rag is completely damp and excess liquid can be wrung from the rag. The wringing serves to remove excess liquid and to distribute the chemicals more evenly throughout the rag. The remaining nitric acid in the rag is then neutralized with a 2.6 M sodium hydroxide solution. This concentration of sodium hydroxide is enough to neutralize the acid and furnish enough hydroxide ion to allow the cerous ion and ferric ion to precipitate as hydroxides while requiring the same volume as the ceric/nitric decontamination solution and ferrous sulfate solution.

The steps in this process are easy to implement and verify in the field. The decontamination solution changes the rag color to an orange shade typical of ceric solutions. The ferrous sulfate solutions changes the color back to the towel color (cerous ion is colorless) with a shift toward the beige due to the ferrous. Addition of the sodium hydroxide turns the towels dark bluish green, but this color turns to the red-orange of rust as the compounds change mostly to oxides during drying. The color changes allow workers to see how well the chemicals have covered the rags and mixed together.

Waste Handling

The PFP gloveboxes have a port with a 12 mil polyvinyl bag attached to seal out waste. The port size varies from 8 to 36 inches, and typical sizes are 8, 11, and 15 inch diameter. All seal out bags contain NucFil filters on the bag and the drums are vented with NucFil filters which prevent the accumulation of gases within the drum or storage boxes. Depending on the path of waste from the glovebox to the drum, there may be an additional vented bag(s) placed over the original sealout bag. In all cases, a vent path is maintained.

Waste drums are limited to a maximum of 1% free liquids. To assure this, additional absorbent (such as kitty litter or zeolite) is typically added. Wet and wrung-out rags are satisfactory to put into a waste package. The drum or storage boxes can contain multiple bags of sealed out waste. Drums with contents designated as "corrosive" have a 90 mil polyethylene liner. The maximum practical loading (from PFP experience) is 66 pounds (30 kg) of rags, although a more typical loading would be about 33 pounds (15 kg) of rags per drum. Inside each seal out bag there will be some air space. Additionally, there are air spaces between the individual packages and between the drum or storage box sides. These air gaps limit the heat rejection capabilities of the drum or storage boxes.

Once the drums are loaded they are stored temporarily at PFP until they can be shipped to Hanford's Central Waste Complex (CWC). The envisioned storage condition at PFP would be outside unshielded in open air. Once the drums are at CWC, they are stored on metal pallets with four drums to the pallet and then stacked three high making for a two by two by three configuration. Two sides of the drum must be accessible for waste inspections. The drums at CWC are stored in a enclosed building but without temperature control.

Testing Strategy and Scope

The objective of the investigation is to develop a strategy for any implemented decontamination approach that will assure safe conditions during decontamination and during the disposal of the residual wastes. The approach has involved

- Laboratory thermal sensitivity testing to identify the combinations of decontamination materials that can react and generate heat sufficient to lead to self-heating reactions
- Quantifying the heat liberated in those exothermic reactions
- Defining the limiting thermal conditions for the exothermic reactions
- Analyzing the waste packaging to predict transient and equilibrium temperatures
- Evaluation of alternative absorbent materials and conditions

For each of these chemical options, several additional conditions were identified that may influence the potential for self-heating reactions. These include

- Rag material (cotton or various synthetics)
- Percentage of excess water remaining on the rag
- Age of the rag after treatment with decontamination chemicals

Initial testing found that cotton rags used with the cerium nitrate that had been reduced with ferrous sulfate and neutralized with sodium hydroxide and allowed to air dry had a low temperature exothermic reaction close to ambient temperatures. That was a surprising result, because the reduction and neutralization steps were expected to create a non-reactive condition. Additional tests were then designed to understand the separate effects of each component in the system and to identify an approach to eliminate reactions at potential storage temperatures, including cerium nitrate/nitric acid, ferrous sulfate, sodium hydroxide, oxygen, and rag composition.

Testing results confirmed that the exothermic reactions were occurring between the nitric/nitrate ion and the cellulose of the cotton rag. Because of complexity of nitric/nitrate ion acid and cellulose reactions (hundreds are possible), testing was conducted to determine the effects of aging.

Testing was conducted using cerium nitrate solutions with synthetic material (50% nylon, 50% polyester) to confirm expectations that the nitric/nitrate ion reaction with these materials would be less energetic and less thermally sensitive.

Thermoanalytical Testing Methods

Two thermoanalytical methods were used to determine the thermal sensitivity of simulated rag wastes from glovebox decontamination:

- differential thermal analysis (DTA)/thermogravimetry (TG) used to measure enthalpy and mass changes for 1 to 1000 mg samples as the temperature was increased at a controlled, known rate in a flowing gas stream, and
- an accelerating rate calorimeter (ARC) which is an adiabatic calorimeter that measures self-heating rates and pressure after the sample is heated to an operator-selected temperature.

DTA/TG is typically used to screen potentially reactive chemical systems for heat-producing reactions which could affect operations safety. These methods can also be used to obtain reaction kinetics and enthalpies (ΔH), particularly for endothermic (heat-requiring) reactions. Measurement of enthalpies for exothermic or heat-producing reactions is complicated by removal of gas reaction products and reaction heat by the flowing gas purge resulting in a less-than-quantitative enthalpy measurement.

The ARC is often used after performing thermodynamic calculations to estimate the potential reaction energy density and/or DTA evaluation of the system's potential thermal reactivity and sensitivity. Because the ARC is a constant volume system, energy change (ΔE) can be measured as opposed to enthalpy (heat) change obtained with DTA or a differential scanning calorimeter (DSC) which is another method similar to DTA.

The testing results of the DTA and ARC showed excellent correlation. This allowed the DTA to be used for quick screening tests and optimized the usage of the ARC, which is more time consuming.

Results from Testing and Analysis

Tests were conducted on cerium nitrate solutions with cotton and synthetic rags. In addition, the effects of rag age (after treatment with decontamination and neutralization solutions) were evaluated. Heat generated by the cerium-cotton combination was modeled as it would be packaged in drums to provide insight to the temperatures that will be generated inside the waste package. These results and analyses are presented in the following sections.

Thermal Sensitivity of Cerium Nitrate and Cotton Rags

We first discovered that air-dried ferrous-reduced and hydroxide-neutralized ceric nitrate and nitric acid rags reacted exothermically at or near room temperature in DTA screening studies. Fig. 1 provides the DTA-measured thermal behavior of cerium nitrate/nitric acid, reduced, and neutralized on cotton. The initial starting temperature for the first exothermic reaction was 20°C. This observed behavior suggests that storing cotton rags resulting from the ceric nitrate decontamination process at ambient Hanford temperatures could self-heat to temperatures (~200°C) where very rapid exothermic reactions occur unless this heat is mitigated.

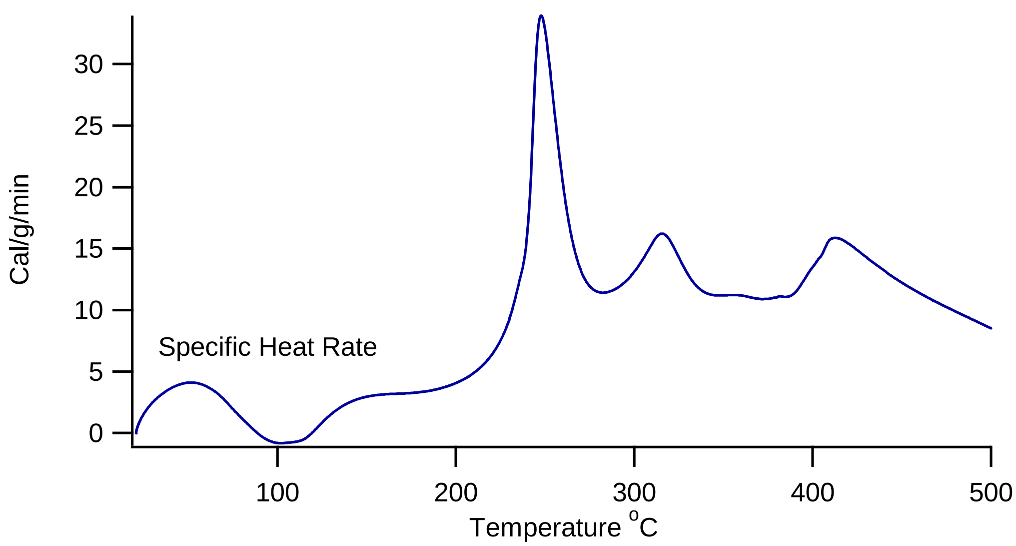

Fig. 1. Thermal behavior of reduced and neutralized cerium nitrate/nitric acid on cotton

To further assess the potential hazard from the ambient temperature exothermic reaction, the same rag was analyzed the following week on the ARC. As Figure 2 shows, the ambient or near-ambient (65°C) temperature exothermic reaction can under adiabatic conditions heat the neutralized and reduced rag to up to a temperature (240°C) where the reaction rate accelerates rapidly leading to an over-pressurization of the sample container.

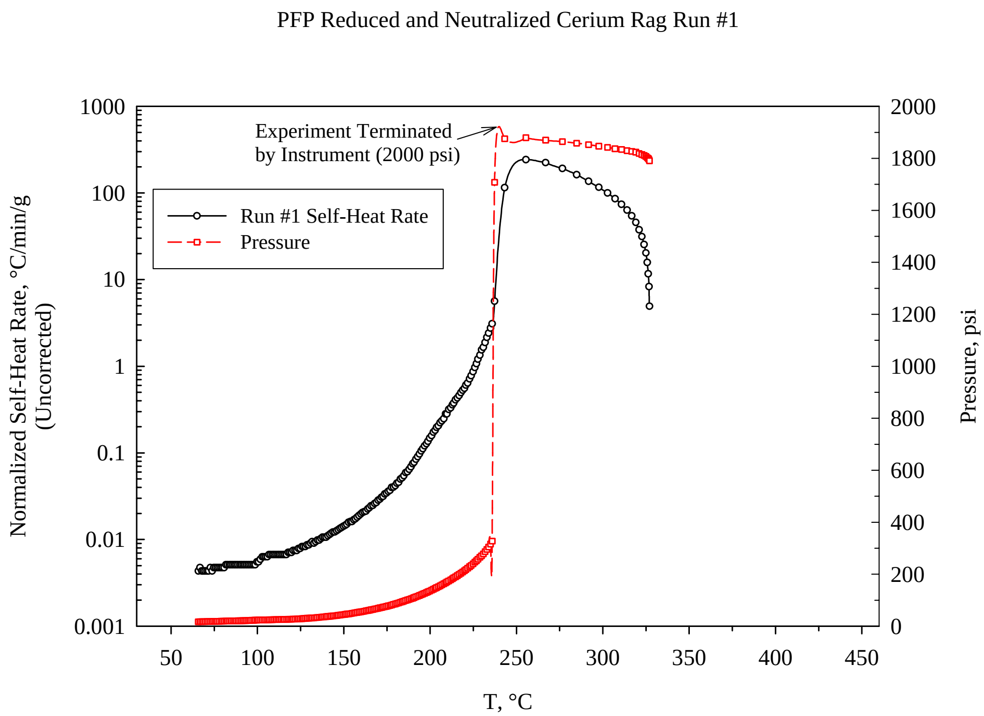

Fig. 2. ARC analysis of Cerium Nitrate on cotton

Aging Effects of Cerium Nitrate on Cotton

The reaction between the nitric/nitrate ion and cellulose is very time dependent (aging) because of the complexity of the reactions as shown in Figure 3. When the material is young, the near-ambient reactions are strongly endothermic but become exothermic as the rag ages later becoming endothermic again. These studies indicate that as this material ages, it will initially become more reactive at ambient temperatures raising the potential for the rapid 200°C reaction to occur but after aging 146 days the low temperature reactions appear spent and unable to raise the temperature where the 200°C reaction can begin.

To assure the safety of less than 146 days cerium nitrate rags once packaged in drums, the storage system must effectively transfer the low temperature exothermic reaction heat from the drum or else the drum’s internal (centerline) temperature will continue to increase until the second exothermic peak begins. After the second exothermic reactions begin the drum temperature will then be high enough to consume the reactants. After 146 days such precautions appear unneeded.

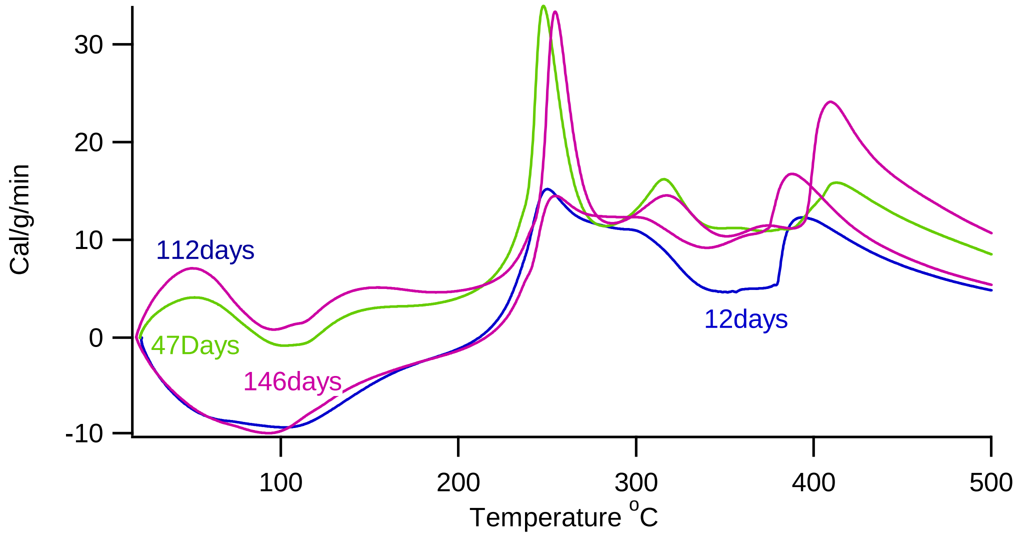

Fig. 3. DTA analysis of Cerium on cotton as a function of time*

* Cotton towel treated on 03/10/04 (HNO3 & Ce(NO3)4 + NaOH + Fe^{++})
Days in Figure 3 refer to elapsed time between exposure and analysis

In this graph between ambient and 200°C, we see endothermic reactions for the 12 day and 146 day rag. This means that the rags absorbed heat in that temperature region. Between 47 and 112 days, exothermic reactions are observed within the same temperature region, indicating that the rags are net emitters of heat. The exothermic display between 47 and 112 days, is a result of various reactions between the nitrate ion and the cellulose, however the chemistry is not understood well enough to identify the specific reactions occurring at this low temperature.

Between 200 and 300°C, a small exothermic peak is observed for the 12 day and 146 day rag, however very large exothermic peaks are observed for the 47 and 112 day rags. This exothermic energy is the result of nitrates reacting with the cellulose. It is surmised that reactive gases are emanating from the nitrate salts to cause this reaction. The most probable gases are HNO_3, NO_2 and NO.

Between 375 and 500°C additional exothermic peaks are observed. These peaks correspond to the known temperatures at which pyrolysis and thermal decomposition of the cellulose occurs. It is therefore understandable why additional exothermic reactions are observed in this temperature range.

As the ceric nitrate cotton rags age the risk associated with them increases then diminishes as the reaction enthalpy increases and then declines as the rags age. As measured by the DTA, the low temperature reactions (20-120°C) are endothermic at 12 days old. The low temperature reactions become exothermic between 47 and 112 days, and return to endothermic at 146 days. Reactivity at the higher temperatures is also low at the beginning and end with maximum reaction energetics seen at 47 to 112 days.

Thermal Modeling of Cerium Nitrate on Cotton

To gain a greater understanding of the reactivity risk associated with the laboratory results showing that slow exothermic reactions do take place at room temperature when cerium nitrate is used with cotton rags, the thermal behavior of a nominal drum containing cerium rags using initial reaction rates was modeled.

The insulating effects of packaging is of concern because packaging affects may result in unacceptable temperatures if even a small heat generating reaction is taking place inside a waste drum. If drum temperatures were allowed to reach about 180°C, a runaway reaction could result. The objective of the thermal modeling is to estimate the internal temperature distribution of a drum loaded with cotton rags used for decontamination with cerium nitrate solution.

The modeling was conducted using two- and three-dimensional numerical simulations of drums arranged in a 3x 3 array. The key assumptions included:

Heat load (from chemical reactions)	=	125 watts
Mass load of rags in drum	=	66 pounds
Effective thermal conductivity of rags in bags	=	0.046 Btu/hr-ft-°F
Ambient temperature	=	45°C (113°F)
Natural convection only		
Drum surface radiation neglected (no solar insolation)		
No evaporative heat loss		

Figure 4 shows how the maximum (centerline) temperature of the drum increases as more rags are packed inside. During the period that the rags are reacting with the residual decontamination solution, each rag contributes a small amount of heat to the drum. A typical fully loaded drum would be predicted to generate about 125 watts.

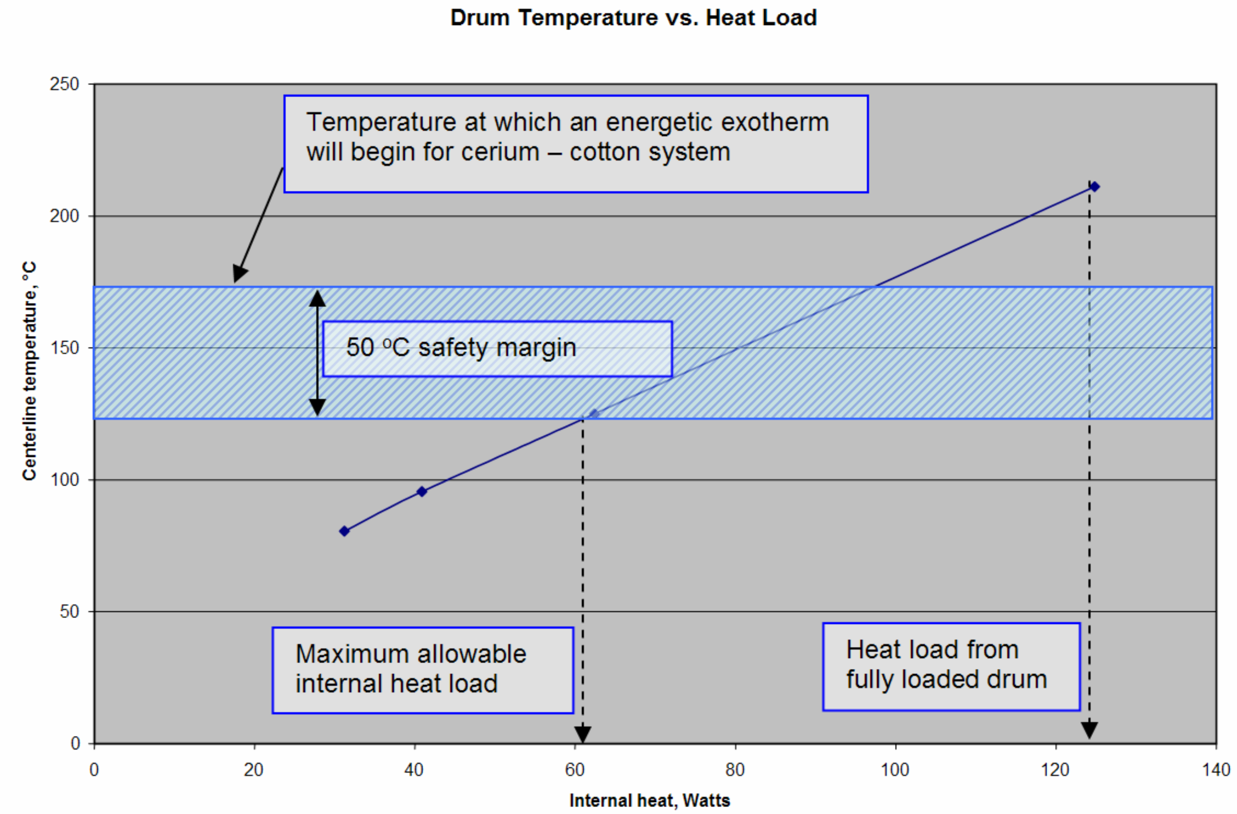

Fig. 4. Predicted temperature for drum of Cerium-cotton waste

Clearly, a fully loaded drum will cause the temperature to rise to the point where the energetic reaction begins (about 180°C). Even half loaded with rags, the internal heat generation will cause the temperature to rise to unacceptably high levels. As such, it was concluded that a safe configuration could not be guaranteed if heat generating reactions were occurring within the drum at expected storage conditions. Efforts were then focused on finding combinations of rag materials and decontamination solutions that would not self-heat, and the modeling effort was discontinued.

Thermal Sensitivity of Cerium Nitrate and Synthetic Rags

The exothermic reactions taking place on the cotton rags appeared to be a reaction between the cellulose and the nitrate ion. In a successful attempt to eliminate this reaction, a series of tests using synthetic rags was conducted to examine that hypothesis.

In neither the DTA nor the ARC data was there observed an exothermic reaction for the cerium nitrate on synthetic rag until a temperature of about 200°C and 160°C, respectively. The sharp exothermic reaction observed by the DTA peaking at about 250°C could release a significant amount of energy if it were to occur, but the required temperatures are well above expected storage conditions at Hanford. The differences between the DTA- and ARC-observed onset temperatures are typical with the increased sensitivity of the ARC.

The neutralized and reduced ceric nitrate synthetic rags, do not exhibit ARC-detectable thermal reactivity until 160°C, well-above possible storage temperatures at Hanford. This safety margin is much more than the normal 50°C safety margin used to assess process operational risks.

Conclusions

Cerium Nitrate has been proposed for use in the decontamination of plutonium contaminated equipment at the Plutonium Finishing Plant located on the Hanford Nuclear Reservation in eastern Washington. A Treatability Study was conducted to determine the validity of this decontamination technology in terms of meeting its performance goals and to understand the hazards associated with the use of Cerium Nitrate under the conditions found at the PFP.

<u>Cotton rags used with cerium nitrate</u>

- Will remain reactive and generate heat even after they have been treated with neutralizing and reducing reagents
- A slow heat-generating reaction proceeds at room temperatures, but a much more energetic reaction starts if temperatures rise above 70°C
- As the rags age, the temperature at which a self-heating reaction occurs gets slightly lower
- When the dry rags are about 18 weeks old, they no longer exhibit ambient temperature self-heating reactions
- Wetting the rags will add a margin of safety
- Wet rags show no <u>net exothermic reaction below 100°C.</u>

<u>Synthetic rags used with cerium nitrate</u>

- Do not self heat at ambient temperature.

Consistent with industry practice, a safety margin of 50°C should be maintained between the highest temperature a potentially reactive material will reach in the process, and the ARC-measured onset temperature for an exothermic reaction. For the decontamination system, the highest temperatures will occur in the waste drums during storage. The waste package (drum) can be maintained in a safe configuration by:

- Using synthetic rags with cerium nitrate (This avoids having to maintain the rags wetted).
- Assuring that adequate moisture is included in the waste package to keep the rags moist for at least 18 weeks as an added safety precaution.
- Assuring the waste drums are not subjected to high external heat loads, such as direct sun on hot days.

REFERENCES

[1] Guide for Conduction Treatability Studies Under CERCLA, Interim Final, EPA/540/2-89/058, December, 1989