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Safety Studies to Measure Exothermic Reactions of Spent Plutonium Decontamination Chemicals Using Wet and Dry Decontamination Methods

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SAFETY STUDIES TO MEASURE EXOTHERMIC REACTIONS OF SPENT PLUTONIUM DECONTAMINATION CHEMICALS USING WET AND DRY DECONTAMINATION METHODS

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ABSTRACT

The Plutonium Finishing Plant (PFP) at the Hanford site in Eastern Washington is currently being decommissioned by Fluor Hanford. 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 and sequestering agents. Aggressive chemicals are commonly used to remove transuranic contaminants from process equipment to allow disposal of the equipment as low level waste. Fluor's decontamination procedure involves application of chemical solutions as a spray on the contaminated surfaces, followed by a wipe-down with rags. Alternatively, a process of applying oxidizing Ce IV ions contained in a gel matrix and vacuuming a dry gel material is being evaluated. These processes effectively transfer the transuranic materials to rags or a gel matrix which is then packaged as TRU waste and disposed.

Fluor is investigating plutonium decontamination chemicals as a result of concerns regarding the safety of chemical procedures following a fire at Rocky Flats in 2003. The fire at Rocky Flats 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. Although the investigation of the fire was not conclusive as to cause, the reviewers noted that rags were found in the glovebox, suggesting that the combination of rags and chemicals may have contributed to the fire. Because of this underlying uncertainty, Fluor began an investigation into the potential for fire when using the chemicals and materials using wet disposition and dry disposition of the waste generated in the decontamination process and the storage conditions to which the waste drum would be exposed. The focus of this work has been to develop a disposal strategy that will provide a chemically stable waste form at expected Hanford waste storage temperatures. Hanford waste storage conditions are such that there is added heat to the containers from ambient conditions during storage especially during the summer months.

Treatability tests under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) were used to assess the use of certain chemicals and wipes (wet method) and chemical-gel matrices (dry method) during the decontamination process. Chemicals being considered for decontamination of gloveboxes at PFP include cerium (IV) nitrate in a nitric acid solution, and proprietary commercial decontamination agents such as RadPro\textsuperscript{TM}, Glygel\textsuperscript{TM} and ASPIGEL 100\textsuperscript{TM}.\textsuperscript{3} As part of the treatability study, Fluor and the Pacific Northwest National Laboratory (PNNL) personnel have evaluated the potential for self-heating and exothermic reactions in the residual decontamination materials.

From these wet and dry method treatability studies, certain limiting conditions have been defined that will aid in assuring safe operations and waste packaging during the decommissioning and waste disposition process.
INTRODUCTION

Fluor Hanford is decommissioning the Plutonium Finishing Plant (PFP) at the Hanford site. Aggressive chemicals are commonly used to remove transuranic contaminants from process equipment to allow disposal of the equipment such as gloveboxes as low level waste. Fluor has determined that some of these spent chemicals on wipes or in a gel matrix can pose an unacceptable self-heating risk in waste containers under certain conditions.

Treatability studies under CERCLA were used to assess the use of certain chemicals and wipes during the decontamination process. The processes included both wet deposition of waste and dry deposition of waste. The wet deposition process included chemicals such as Cerium (IV) nitrate in a nitric acid solution, and proprietary commercial solutions such as RadPro™ that include acids, degreasers, and sequencting agents. The dry deposition process included the use of proprietary chemicals such as Glyge™ and ASPIGEL 100™.

Fluor’s wet decontamination process 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. Fluor’s dry decontamination process involves the application of proprietary chemical gels that when dry are vacuumed or swept as dry particulate with the waste adhering to the gel.

Treatability Tests

Treatability studies under CERCLA 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 a site. Consequently a treatability study was determined to be important in determining the effectiveness and safety of using Cerium Nitrate and RadPro™ 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. An additional treatability study was performed on a non contaminated mockup to determine if a dry matrix of gel/chemical/waste resulting from the proprietary chemicals Glyge™ and ASPIGEL 100™ would provide a suitable waste matrix for storage conditions at Hanford temperatures.

These studies were performed to determine the implementability of the wet and dry decontamination processes and determine the safety of their use in the field. There was a concern that using the Cerium Nitrate and other similar chemicals at PFP such as RadPro™, Glyge™ and ASPIGEL 100™ could result in self-generation of heat and possibly result in a fire during the removal process or while the waste was stored on site in drums. Treatability studies were needed to determine performance information with regard to waste types, types of wipes and types of chemical media to be used, if a wet process was safer than a dry process and to model conditions that could be problematic for waste storage in the field.

As many as three tiers of treatability testing may be performed: laboratory screening, bench-scale testing and pilot scale testing. Laboratory testing 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.

Thermal reactivity treatability studies were performed in the laboratory as bench-scale tests. An additional bench scale test was conducted by a CEA laboratory on ASPIGEL 100™ to confirm safe disposal with larger quantities and materials.

Proposed Decontamination Methods: Wet Method

Two wet methods have been evaluated at PFP: Cerium IV Nitrate solution and RadPro™ solution. 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
- Waste drums are stored outside until transported to an on-site interim storage facility

The cerium nitrate decontamination method involves spraying a solution of 0.25 molar ceric nitrate in 1 molar nitric acid onto the walls of a glovebox, allowing it to 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.

The RadPro™ decontamination process uses proprietary chemicals which are applied in a specific sequence:

- A buffered acidic degreaser (75% RadPro™ 02, 25% RadPro™ 03) is sprayed onto the glovebox interior surfaces and lightly scrubbed.
- After the specified dwell time, the interior is thoroughly rinsed with a nitric acid-based rinsate solution (10% RadPro™ 03, 90% demineralized water). The process is repeated as necessary and the residual liquid is absorbed on cotton towels, neutralized with sodium carbonate, and packaged as waste.
- An emulsifying solution (RadPro™ 01) is then sprayed onto the glovebox interior surfaces and allowed to dwell.
• After the specified dwell time, the interior is thoroughly rinsed with the rinseate solution. The process is repeated as necessary and the residual liquid is absorbed on cotton towels, neutralized with sodium carbonate and packaged as waste.

Waste Handling

The FFP gloveboxes have a port with a 12 mil polyvinyl bag attached to seal out waste. All seal out bags contain small HEPA filters on the bag and the drums are vented with HEPA filters which prevent the accumulation of gases within the drum or storage boxes. Thus, a vent path is always maintained.

Wet and wrung-out rags are satisfactory to put into a waste package; kitty litter or zeolite is added to assure no free liquids. 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. The air spaces within and between the individual packages and between the drum or storage box sides limit the heat rejection capabilities of the drum or storage boxes.

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

Testing Strategy and Scope for Wet and Dry Methods

The objective of the investigation was to develop a strategy for any implemented chemical 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 or exothermic 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
- Evaluating alternative absorbent materials and conditions

For each of these chemical options, several additional conditions were identified that could 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
- Dried gel matrix

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. Testing results confirmed that the exothermic reactions were occurring between the nitric/nitrate ion and the cellulose of the cotton rag. This can be problematic in terms of the initiation of combustion in the waste drum. Testing was also 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.

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

Air-dried ferrous-reduced and hydroxide-neutralized ceric nitrate and nitric acid rags reacted exothermically at or
near room temperature in DTA screening studies. Figure 1. Thermal Behavior of Reduced and neutralized Cerium Nitrate/Nitrile Acid on Cotton provides the DTA-measured thermal behavior of cerium nitrate/nitrile 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.

Analysis after one week of storage indicates, as Figure 1 shows, that 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.

Thermal Sensitivity of Cerium Nitrate and RadPro™ 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.

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

The initial implementation plan for the RadPro™ decontamination process was to use cotton rags to remove the decontamination solutions. Because of the success from using synthetic rags with the ceric nitrate process, synthetic rags were also tested. Testing was done with the RadPro™ solutions with both cotton and synthetic rags to provide examples of the combinations that would exist in actual use of the product.

The results of DTA screening studies of dried cotton rags soaked with RadPro™ indicate that any exothermic behavior occurs after 110°C following an initial endothermic reaction for all of these tested materials. ARC analysis indicates that a cotton rag soaked in the RadPro™ decontamination solution begins to react at about 60°C. This behavior is similar to that observed for the cerium nitrate/nitrile acid cotton rags and indicates that these RadPro™ cotton decontamination rags have a high potential to begin reacting at ambient temperatures.

A synthetic rag soaked with RadPro™ decontamination solution, begins to self-heat at about 80°C.
This observed onset temperature is again too near possible ambient temperatures to provide the safety assurance desired. Neutralization of the residual nitric acid to reduce the reactivity was then tested.

Cotton rags were soaked with RadPro™ decontamination solution and neutralized with sodium hydroxide to a pH near 12. The ARC observed no self-heating reactions for the neutralized rag until 180°C. These results indicate that neutralization of RadPro™ solution saturated rags should provide the desired 50°C safety margin from expected ambient storage conditions.

The Importance of Rag Moisture as a Mitigating Effect

During the exothermic phase of the nitric/nitrate-cellulose reaction a way to absorb the energy of these reactions is needed. Given the low rate of the exothermic reaction, the addition of water seemed an obvious solution. Testing of a rag moistened with water confirmed that that would be more than enough water to absorb the exothermic energy. Calculations showed that there was more than enough water if the rags were wetted such that the latent heat of vaporization would absorb all the low energy exothermic reactions inside of drums while stored until the reaction turned endothermic. A small quantity of water will provide a substantial factor of safety in preventing high temperatures that could initiate energetic reactions.

Conclusions for Wet Method

Cotton rags used with decontamination agents containing nitric/nitrate ions
- 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 net exothermic reaction below 100°C.

Synthetic rags used with cerium nitrate
- Do not self heat at ambient temperature.

Cotton or Synthetic rags used with RadPro™ Solutions
- An exothermic reaction can occur with the decontamination solution if the temperature rises to about 150°C, but the reaction is independent of the rag material.

RadPro™ solutions can be safely used with either cotton or synthetic materials, but care must be taken to assure the decontamination solution (alone) does not reach temperatures above about 80°C. If the solution is neutralized, this temperature can be raised to 150°C.

The Dry Waste Deposition Decontamination Method: Use of Chemical/Gel Matrix

For gloveboxes that are deeply etched with plutonium contamination, methods of applying Cerium Nitrate contained in gels are being evaluated. Gel methods allow the decontamination chemicals a longer reaction time on the metal surfaces thus increasing the etching depths of the chemicals into the steel. This improves fixed decontamination. After drying, the gel turns to dry particulates that trap the radioactive contaminants and that are collected by brushing and vacuuming. Samples were collected in a filtered vacuum cleaner. The Glygel™ and vacuum filters were collected and submitted as samples. For the ARC analysis, dried Glygel™ and the two types of filter media were weighed to determine relative ratios. ARC samples were then prepared using the same ratios.

Glygel™ is a decontamination product composed of decontamination chemicals (Ce IV, nitric acid), organic surfactant and gel. Self heating was observed in the Glygel™ tests and is postulated to arise from reactions with the surfactant. Differences in low temperature reactions observed with and without surfactant in dried Glygel™ ARC tests indicate that some surfactant or reactive fragments of surfactant survive the application and drying process. Without surfactant, self-heating is not observed in the ARC below about 175°C as compared to reactions at temperatures as low as 65°C with surfactant in the Glygel™.

The first ARC analysis of dried Glygel™ consisted of a 1 g sample heated to 200°C. Self-heating was observed starting at 116°C. Self-heating was observed at 81°C for a 3 g sample of the same material. This sample was heating rapidly when the sample container failed to maintain pressure at 250°C. The 3 g sample reaction beginning at 80°C stops which likely would not be the case for a larger sample.

To test the effect of surfactant on Glygel™ reactivity, two samples were prepared using Glygel™ with and without surfactant. The Glygel™ was transferred into the bottle containing the surfactant and mixed. The mixture was then painted onto sheet metal. The sheet of stainless steel with the Glygel™ coating was allowed to dry completely in a hood.

ARC testing of the Glygel™ with and without surfactant samples were completed. Low temperature self-heating was again observed for the samples with surfactant. For the samples prepared without surfactant, self-heating was not observed until 176°C.

In Figure 3, a self-heating reaction is detected at 80°C and continues until the analysis was terminated at 115°C due to the rapidly increasing temperature rise.

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Because of demonstrated chemical reactions of Glygel™ with surfactant producing an exothermic reaction, an alternative decontamination gel was investigated for use at FFP. This decontamination gel is called ASPIGEL 100™. It is composed Cerium IV Nitrate, nitric acid and gel forming matrix and no organic surfactant. ARC testing was performed to determine the thermal reactivity sensitivity of ASPIGEL 100™ under potential storage conditions on the Hanford site. Testing revealed that 3 g of ASPIGEL 100™ alone could not support a self-sustaining reaction beginning near 70°C up to 185°C where a more rapid self-sustaining reaction is observed to occur; this second reaction produces 140 psi of gas at 210°C. In the initial test of 10 g of ASPIGEL 100™ alone, the sample was heated to 100°C. The results determined that 10 g of ASPIGEL 100™ supports a self-heating reaction to 100°C under adiabatic conditions. With this indication that 10 g of ASPIGEL 100™ will support self-heating to within 85-90°C of the faster reaction, another experiment was conducted with 10 g of ASPIGEL 100™ to 140°C which is within 50°C of the second reaction's onset.

Similar thermal reactivities are found for the two 10-g ASPIGEL 100™ experiments to 100°C and 140°C. The second experiment to 140°C shows that ASPIGEL 100™ can self-heat to within 50°C of the second reaction's ARC-observed onset temperature; a >50°C safety margin between the needed operational temperature and the ARC-observed onset temperature is a chemical-industry rule-of-thumb.

In the 140°C experiment, the reaction accelerates to slightly above 100°C and then begins to slow. Simultaneously with the slowing of the reaction, the rate of pressure increase increases more rapidly suggesting that an endothermic mass loss is occurring such as evaporation of loosely bound water (mass 18 g/mole). This theory is consistent with PFP's observation that gaseous mass 18 is produced between 70 and 200°C.

Analysis shows that even with this endothermic reaction, sufficient heat is produced to continue to self-heat the ASPIGEL 100™. If the evolved gas is water, the amount of water present may vary from one batch of ASPIGEL 100™ to another depending on the preparation and storage conditions. In summary, our one experiment to within 50°C of the onset of the second more rapid thermal reaction observed for ASPIGEL 100™, indicates that there is sufficient heat produced by the initial reaction to raise the material's temperature to 140°C under adiabatic conditions. This experiment should provide the worst case behavior.

To determine if the low energy reactions would be a problem at the planned volumes required by field work, and to test the impact of large material quantities, a bench scale study designed to approximate field conditions was conducted at a CEA laboratory. A vacuum cleaner filled with 1.5kg of dried ASPIGEL 100™ flakes was placed into dual layers of vented poly bags and heated to 55°C constant temperature for 7 consecutive days. Temperatures inside the simulated waste package were continuously monitored by a thermocouple and indicated no exothermic reactions occurred during this test.

Figure 3:
Dried Glygel™ with filter media from vacuum cleaner and TGA

Reactions of Glygel™ with cotton rag were also measured. A self heating reaction is detectable at 106°C with a rapid rise in both temperature and pressure observed. Towels used for wipes represent a challenge in analysis due to the variable amount of Sodium carbonate decahydrate used for wipes represent a challenge in analysis due to the variable amount of used for wipes. It is apparent that a different mitigation of hydration could occur at low temperature for the surfactant although none was observed without the addition of heating range examined. The low temperature exothermic reaction observed in the ARC analysis shows as an exotherm in surfactant. Glygel™ without surfactant and sodium carbonate reacted much the same as Glygel™ with surfactant without the addition of sodium carbonate. The ARC testing indicates that mixing and diluting Glygel™ with sodium carbonate does not mitigate the low temperature reactivity of Glygel™.

TGA analysis displayed of dried Glygel™ with surfactant show at least four exothermic reactions during the heating range examined. The low temperature self-heating reaction observed in the ARC analysis shows as an exotherm in the DTA. ARC and TGA testing indicate that Glygel™, a candidate glovebox decontaminating agent for FPF gloveboxes is susceptible to low temperature (near storage temperatures) exothermic reactions. These low temperature gas-producing reactions increase the potential for pressurizing containers of spent Glygel™ waste stored on the Hanford site.
Conclusions

Four candidate chemical decontamination technologies are being considered for decontaminating plutonium contaminated gloveboxes at Hanford's Plutonium Finishing Plant. These technologies are cerium nitrate/nitric acid, EAI corporation's RadPro™ (Wet Method Decontamination) STM1's Glygel™ Decontamination process and CEA/COGEMA's ASPIGEL 100™ (Dry Method Decontamination). PFP and PNNL have and are investigating chemical reactivity hazards of wastes arising from these technologies as they are applied in the field.

Testing at PFP and PNNL found rags used in cerium nitrate decontamination methods showed a low rate exothermic reaction on the dried spent cotton rags starting in the 30°C to 40°C range that could lead to waste drum overheating. This heat is a result of reactions between the cotton rags used to wipe up the solution. The reaction energies were found to change over time. As observed using differential thermal analysis, the low temperature reactions are initially endothermic, become exothermic after several weeks and remain so for weeks then return to endothermic. The addition of moisture to the rags absorbed the energy of the exothermic reactions and will prevent overheating of the waste drums. Additional testing showed that the use of synthetic polyester-nylon rags prevented the low temperature exothermic reactions.

The testing of RadPro™, a proprietary decontamination system from EAI Corporation demonstrated that these solutions produced spent rags that could be stored under current Hanford storage conditions and that neutralization of the solutions dramatically increased the safety margin.

Results from the testing of Glygel™ decontamination products via ARC and TGA testing indicate that Glygel™, a candidate glovebox decontaminating agent for PFP gloveboxes, is susceptible to low temperature (near storage temperatures) exothermic reactions. Low temperature gas-producing reactions increase the potential for pressurizing the waste containers during storage at ambient conditions at Hanford.

Results of the ASPIGEL 100™ testing showed that for amounts of spent gel postulated for field storage conditions, the spent gel waste would not undergo a problematic exothermic reaction in the storage drums at PFP.

REFERENCES


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