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| Author(s): | Hypes, Philip A. |
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# White Paper on Potential Hazards Associated With Contaminated Cheesecloth Exposed to Nitric Acid Solutions

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## Executive Summary

This white paper addresses the potential hazards associated with waste cheesecloth that has been exposed to nitric acid solutions. This issue was highlighted by the cleanup of a 100 ml leak of aqueous nitric acid solution containing Heat Source (HS) plutonium on 21 June 2016.

Nitration of cellulosic material is a well-understood process due to industrial/military applications of the resulting material. Within the Department of Energy complex, nitric acids have been used extensively, as have cellulosic wipes. If cellulosic materials are nitrated, the cellulosic material can become ignitable and in extreme cases, reactive. We have chemistry knowledge and operating experience to support the conclusion that all current wastes are safe and compliant. There are technical questions worthy of further experimental evaluation.

An extent of condition evaluation has been conducted back to 2004. During this time period there have been interruptions in the authorization to use cellulosic wipes in PF-4. Limited use has been authorized since 2007 (for purposes other than spill cleanup), so our extent of condition includes the entire current span of use. Our evaluation shows that there is no indication that process spills involving high molarity nitric acid were cleaned up with cheesecloth since 2007. The materials generated in the 21 June leak will be managed in a safe manner compliant with all applicable requirements.

## Introduction

On 21 June 2016, during glovebox operations, a leak of approximately 100 ml of aqueous solution containing Heat Source (HS) material occurred during transfer of the solution into a precipitation vessel. This leak is a unique event; however, wiping up a few drops from time to time is normal. The leaked solution was cleaned up with cellulosic wipes commonly referred to as “cheesecloth”. The cheesecloths dried due to the presence of HS material and were bagged out of the glovebox and placed into pipe overpack containers (POCs). The leaked solution that was cleaned from the glovebox floor had a nitric acid concentration of 9.8 moles/liter (9.8 M).

Because the cheesecloth, a cellulosic, was exposed to nitric acid, an oxidizer, an evaluation of possible hazards is warranted. Speculation about the event included the potential that when the material becomes waste, it may require classification as RCRA ignitable waste (D001) or RCRA reactive waste (D003). The latter classification is viewed as far less likely. This white paper evaluates the acid/cellulosic interactions that can occur in HS material processing to determine if characteristics of the generated waste may impact the safe handling, storage, transport or disposition of this material.

## Background

In Heat Source (HS) material processing at TA-55, cheesecloth may come into contact with acids during normal operations. Those operations include plutonium purification (plutonium dissolution and oxalate precipitation) and decontamination of the finished fuel clads. The acids used in these processes are nitric acid and hydrofluoric acid.

The cheesecloth used in the HS material operations [5], Fisher Scientific product FIS#06-665-29 is described as:

- Reagent-grade quality
- 100% brilliant white, pure cotton construction will not scratch sensitive surfaces. Has a high degree of cleanliness, softness, absorbency and strength
- Absorb six times their weight in liquids and are useful for mopping up solvents and aqueous solutions
- Inert to even harsh solvents; ideal as filtering material
- Grade 10 (mesh size)
- Each wipe is 18 x 36 in. (46 x 91cm).
- Meets USP and Federal Specification CCC-G-101c.

This report evaluates those interactions to determine any safety issues or potential hazardous characteristics associated with the waste generated. The evaluation includes a review of chemistry literature on mechanisms of cellulosic nitration, reviews of test data for cellulosic material exposed to nitric acid, the chemistry of HS material processing at TA-55, and the US Environmental Protection Agency (EPA) regulatory classifications for hazardous waste, specifically ignitability (D001) and reactivity (D003).

During HS material dissolution and precipitation operations, small spills of reagents and HS solutions can occur. The interactions of these chemicals with cheesecloth were evaluated. No mechanisms were identified in any of the evaluations for appreciable cellulosic nitration. Test data from cellulosic samples exposed to 12 M nitric acid found no evidence of cellulosic nitration [7, 12]. The RCRA code for corrosivity, D002, would not apply to any spills wiped with cheesecloth in HS material operations due to the absence of liquids on the dried rags packaged as waste. RCRA code D003, reactivity, does not apply to any spills wiped with cheesecloth in HS material operations due to the stability of the waste. However, spills consisting of the reagent grade nitric acid at 15.6 M or any aqueous solutions containing dissolved HS material that were absorbed onto cheesecloth can potentially create an ignitable or reactive waste. Tests to evaluate the oxidation potential should be performed using appropriate standardized test methods to determine if the ignitability code, D001, is applicable.

## HS Processing and Materials Discussion

Acids are used in two different HS processes at TA-55, HS material dissolution/precipitation and radiological decontamination of encapsulated HS material. In the dissolution/precipitation process, ~900 mL of 15.6 M nitric acid and ~3.2 mL of 28.9 M hydrofluoric acid are used as the dissolving agents in predefined ratios to the HS material being dissolved [4]. These ratios are predefined for ~180 g of HS material. The hydrofluoric acid is used as a catalyst during the dissolution of the HS material. Once dissolved, the solution is further diluted so that the nitric acid concentration is between 1 M and 2 M. The solution is then treated with urea acid and hydroxylamine nitrate so that the Pu enriched solution has the right chemical properties prior to being precipitated using a solid form of oxalic acid hydrate. Rinsing fluids used throughout the chemical process are 0.1 M nitric acid and De-Ionized (DI) water. Cheesecloth is used to keep the area clean and for equipment decontamination. This helps to keep the background radiation exposure to the process operator As Low As Reasonably Achievable (ALARA).

In the HS decontamination process [3], nitric acid is diluted to 3.5 M and hydrofluoric acid is diluted to 6.4 M. The acids are combined and the encapsulated HS material is dipped into the acid mixture and wiped with water dampened cheesecloth rags to remove external contamination. Each damp cheesecloth is used only once to maximize the decontamination effectiveness. This process is repeated until the radiological contamination is within acceptable limits. The used cheesecloth rags are managed as waste after an MC&A evaluation, and the acid mixture is saved for subsequent use.

## Nitric Acid/Cellulosic Chemistry in General

The main effect of exposing cellulosic wipes and towels to nitric acid is the oxidation and hydrolysis of the cellulose forming lower molecular weight by-products [15, 16]. Cellulosic material can be nitrated with nitric acid if a mechanism exists to generate the nitronium ion ($NO_2^+$) that will electrophilicly attack the hydroxyl oxygen of the cellulose. The most common method of obtaining this nitration reaction is the mixed acid method, in which cellulosic material is reacted with a mixture of nitric acid and sulfuric acid. In the mixed-acid method, sulfuric acid is not consumed, but acts as a catalyst in generating the nitronium ion.

The mixed acid method is not the only method for nitration of cellulose. With anhydrous nitric acid a self-ionization process similar to the mixed acid generation of nitronium can occur when water is not present. When water is present, this self-ionization is unlikely. Nitric acid forms a negative azeotrope with water with a composition of 67.4% $HNO_3$ and 32.6 % $H_2O$ [6]. Negative azeotropes form when two different chemicals react more strongly with each other than they do with themselves. As a result, this greatly reduces the likelihood that nitric acid molecules will interact to self-ionize which is necessary for production of the nitronium ion.

In addition, according to Le Châtelier’s principle, self-ionization of nitric acid is unlikely to occur in the presence of water as reactions are driven in the direction of reactants in the presence of an excess of products. Finally, the chapter *Synthetic Routes to Nitrate Esters,* in *Organic chemistry of explosives*, reports that in the event that nitrate esters are formed (despite the drivers reducing this likelihood), they undergo an auto-catalyzed decomposition resulting in release of nitric acid when exposed to water or moisture [7].

## Nitric Acid/Cellulosic Chemistry, Specifically in HS Processing Operations

In respect to the chemical processes occurring in HS material operations, Hollis [1] performed a detailed analysis of the possibility of other nitrating agents being present in the leaked material that was absorbed with cheesecloth. All these other nitration mechanisms involved reaction mechanisms between one or more species, or reaction conditions for generating the nitronium ion that are significantly different than those found for the reaction of cellulose with solutions used for aqueous recovery of Pu-238.

As discussed previously, nitric acid is known to react with sulfuric acid to form the nitronium ion which is the nitrating agent involved in the formation of nitrocellulose. This process only occurs in the presence of acids that are stronger than nitric acid because in order to form the nitronium ion, nitric acid must act as a base by accepting a proton from a stronger acid to form the intermediate protonated nitric acid that dissociates into water and the nitronium ion. This is the reaction that occurs when nitric acid is mixed with sulfuric acid as the strong acid.

During the HS dissolution process, hydrofluoric acid is added to nitric acid as a catalyst for dissolution of HS material [4]. Hydrofluoric acid, unlike sulfuric acid, is a weaker acid, meaning it is much less likely than nitric acid to dissociate into hydrogen and fluorine ions [8] and does not act as an acid in the presence of concentrated nitric acid to form protonated nitric acid or the nitronium ion. After HS dissolution, the resulting nitric acid concentration is ~ 8 M – 10 M, which is below the concentration at which nitration of cellulose has been observed, as explained in a memorandum to Jeffery Yarbrough from Keith Lacy, NPI-7-16-009, September 1, 2016 [12, 13].

Certain metals can accelerate the nitration process of cellulosic material. In HS material operations, the dissolved HS solution contains numerous trace elements in the 10's to 100's of parts per million concentrations [11]. This is in stark contrast to waste generated from recovery operations such as distillation and evaporation. In those operations, the once trace metals are concentrated such that they drive the chemistry, as is the case for nitrate salt waste. In the waste generated from the dissolved HS material, however, the chemistry is driven by the plutonium and uranium present in significantly higher concentrations, approximately 1 M-2 M [4].

Hollis [1] also considered the possibility of production of viable nitrating species by radiolysis. Though several studies have reviewed the radiolysis of nitric acid/ water systems, none have reported evidence of the formation of the nitronium ion. Her review of intermediates and reaction products identified only two species, $N_2O_4$ and $N_2O_5$, which have been reported to form nitrate esters. It should also be noted that chemical constituents generated by radiolysis are typically in concentrations many orders of magnitude less than those used in the reviewed nitration studies.

Low temperatures are required for nitrate esterification using $N_2O_4$ [7]. At elevated temperatures, as found with Pu-238 solutions, $N_2O_4$ dissociates to $NO_2$ [10]. It also undergoes competing reactions with water producing $HNO_3$ and $HNO_2$ [10]. Consequently, $N_2O_4$ is very unlikely to act as a nitrating agent of cellulose contaminated with materials from Pu-238 due to the heat associated with aqueous scrap processing operations.

Although the nitrating agent $N_2O_5$ is a possible product of radiolysis of nitric acid [9] there are a number of reasons not to expect appreciable amounts of this material to be produced. Therefore it is not expected that appreciable amounts of $N_2O_5$ would be available to react with cellulose to form nitrated cellulose. In aqueous solutions like those under consideration, $N_2O_5$ reacts with water to regenerate nitric acid [10]. In addition it reacts with peroxide ($H_2O_2$) which is a radiolysis product of water to form nitric and peroxynitric acid ($HNO_4$) [10]. $N_2O_5$ also readily volatilizes and in the gas phase it decomposes to $NO_2$ and $NO_3$, the latter of which further decomposes into $O_2$ and NO [10].

## Nitric Acid/Cellulosic Laboratory Testing

Test data on the interactions between nitric acid and cellulosic material is available from testing performed at Rocky Flats in 1995 [2]. During the time of the study, waste forms consisting of cellulose wipes and towels exposed to nitric acid were being stored in drums at Rocky Flats. Concerns were raised about potential nitration of the cellulose waste by residual nitric acid resulting in the formation of a potentially explosive form of nitrocellulose. A study was thus initiated to determine if the cellulose wipes could be nitrated by nitric acid alone, resulting in increased flammability or reactivity of the cellulose material.

The study involved preparation of reference samples of highly nitrated cellulose using nitric acid and sulfuric acid and preparation of cellulose wipe and towel samples exposed in the same manner except in the absence of sulfuric acid. These sample materials were exposed to 12 M nitric acid (considered to be the highest concentration to which the wipes would be exposed), at both room temperature and at 50$^o$ C for different time periods up to 90 days. The reference materials and test samples were then evaluated using a variety of analytical methods. The samples were evaluated using Differential Scanning

Calorimetry (DSC), Thermogravimetric Analysis (TGA), drop-weight impact testing, and hot wire Ignition testing. In addition to the thermal stability testing, the samples were tested for nitration using Fourier Transform Infrared Spectroscopy (FTIR).

The wipes tested were primarily composed of paper (wood) cellulose fibers. Towels were also tested that were primarily made of cotton cellulose fibers. Screening tests were conducted on the towels to determine if the cotton cellulose in the towels could be nitrated. The cellulosic material tested appears to be representative of the cellulosic material present in HS processing at LANL. The nitrocellulose for reference was made, using the mixed acid method (nitric acid with sulfuric acid), with both the wood fiber wipes and cotton fibers from commercial cotton balls.

Impact sensitivity tests were performed using a 6 kg hardened steel anvil dropped from a maximum height of 50cm to impact the sample at rest in a brass sample cup. Each sample that was exposed only to nitric acid tested negative (no detonation) to impact sensitivity. The reference nitrocellulose material tested positive as expected.

Results from FTIR sample tests showed that the spectra from the different nitric acid exposed test material (cotton cellulose, wood fiber wipe cellulose, and cotton towel cellulose) were similar and indicated the basic structure of cellulose. The report states that “no absorption or enhanced absorption bands indicative of nitration were detected.” As expected, nitrate absorption bands were detected for the nitrocellulose reference material along with a decrease in the hydroxide absorption band intensity due to replacement by nitrate groups. Again, no nitration bands were detected for the cellulose samples that were exposed only to the 12 M nitric acid.

In the thermal stability tests, data indicated that the thermal stability of the wipes are decreased upon exposure to nitric acid. However, the temperature at which auto ignition (oxidation) could occur is reduced only nominally. Due to formation of lower molecular weight species during exposure to nitric acid, the decomposition products will volatilize at a lower temperature than the unexposed wipes, which was indicated by weight loss of the nitric acid exposed samples over a lower temperature range. This was the primary TGA result for the residues collected from the nitric acid decomposition of the cellulosic sample materials.

Hot wire tests were performed on the samples. These tests were not equivalent to the DOT and RCRA test methods for ignitability because of sample size, testing arrangement, and time of heating. The hot wire test was performed in one series with the wire at the top of the sample and in another series with the wire at the bottom of the sample. The reference nitrocellulose samples flashed as expected in both arrangements, leaving little residue remaining. The samples exposed only to the nitric acid did not. Some of the acid exposed samples did ignite and burn easier than the unexposed samples which indicate an increase in the ignitability and combustibility characteristics. Since nitration did not occur, this is attributed to the breakdown of the cellulosic into lower weight compounds. These characteristics should be evaluated further through testing.

## Extent of Condition

In order to determine the number of waste drums that may be of concern, records of waste drums were investigated [12]. This investigation was conducted for drums created from 2004 to the present. The databases of record are the Waste Management System (WMS) through 2009, and the Waste Compliance And Tracking System (WCATS) for 2010 to the present.

During 2004-2009, 2,618 drums of transuranic waste were produced at TA-55. Of those drums, 2,190 (83.7%) are currently located at the Waste Isolation Pilot Plant (WIPP). Seventy-four (74) of those drums (2.8%) are located at TA-54. Six drums (0.2%) are located at the Waste Control Specialists facility in Texas. Three hundred and forty eight (348, representing 13.3%) were reclassified as low level waste and dispositioned accordingly. Figure one summarizes this data.

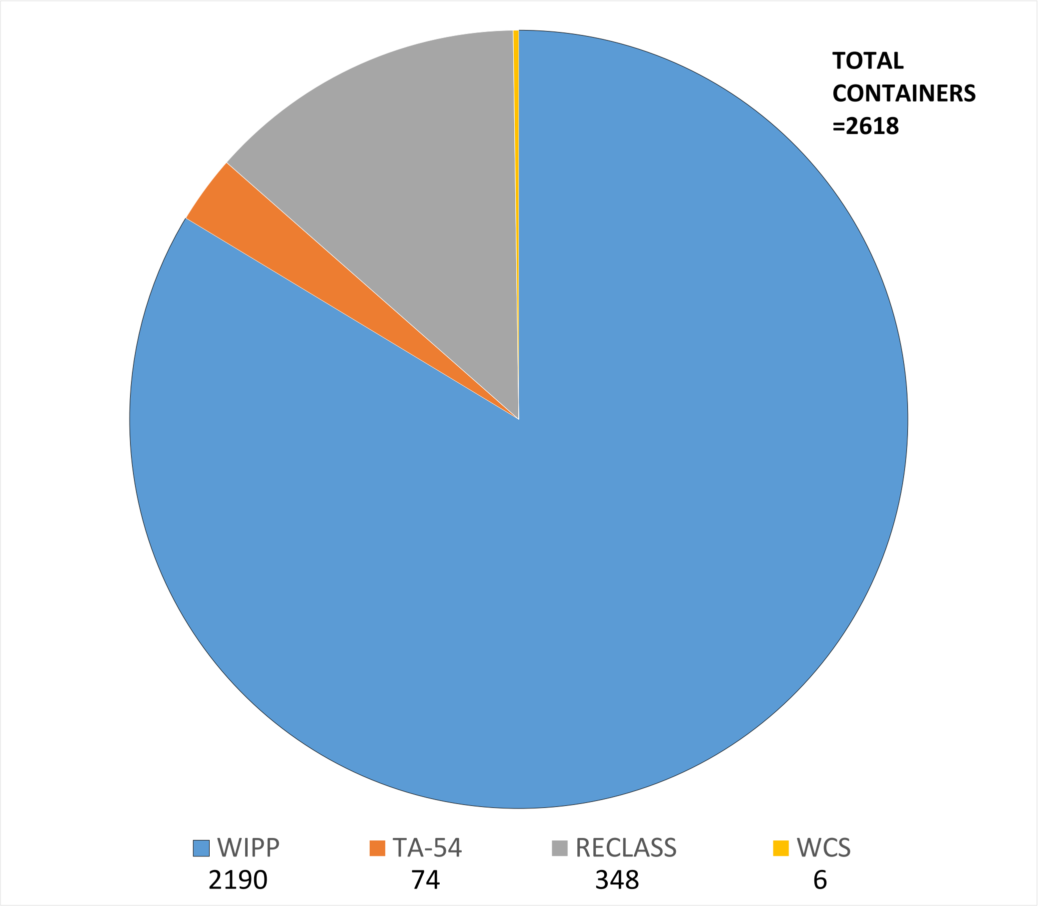

Figure 1. Transuranic waste drums produced at LANL/TA55 2004-2009

For the time period from 2010 to the present, 2513 drums of transuranic waste were generated. While 84 drums were generated from HS material operations that involved high molarity nitric acid, none of those drums involved waste from spill cleanup. The conclusion drawn is that there is no indication that process spills involving high molarity nitric acid were cleaned up with cheesecloth [12]. This indicates that there are no drums in the 2010-present time frame that contain material similar to that created as a result of the 21 June 2016 leak.

Figure two summarizes the current location of the drums generated from 2010 to the date of this white paper.

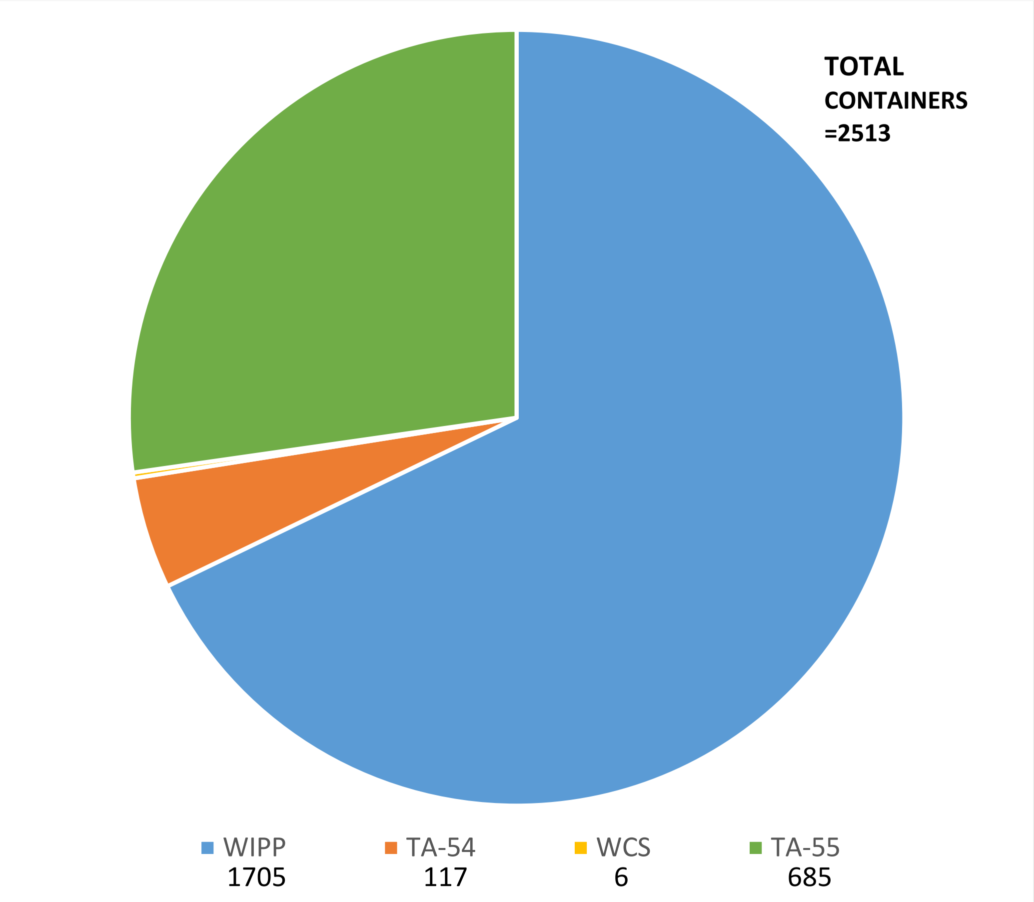

Figure 2. Transuranic waste drums produced at LANL/TA55 2010-present.

The review of WCATS found data on two drums that mention “spill” and “cheesecloth.” One of the two drums’ records also mention “nitric.” These two drums are from $^{239}$Pu areas where high molarity nitric acid is not used. These two drums are currently at WIPP.

## Recommendations

Three broad recommendations to gather further information to fill existing knowledge gaps or to verify expectations have been identified.

1. Evaluate methods for cleanup of solutions with concentrations greater than 10.3 M nitric acid that do not involve cellulosic material. Consideration should be given to alternative absorbents, reduction of acid concentration prior to or after absorbing, or both. Prior to selection of alternative method(s), testing of the generated waste material characteristics should be performed to demonstrate the characteristics of the waste material. For processes that generate transuranic waste, testing and alternative selection should be coordinated with the Carlsbad Field Office (CBFO), and the Difficult Waste/Site Interface Team, Repository Science and Operations at the LANL Carlsbad office. Any methods considered must be evaluated in accordance with OE-3: 2016-05 [14]. Such methods must also be evaluated in order to ensure they do not meet the definition of RCRA hazardous waste treatment. If they do, such treatment would be conducted in a fashion fully compliant with the applicable regulations and/or the facility Hazardous Waste Permit.

2. Perform testing on the Fisher Scientific cheesecloth that is used in HS processing operations to evaluate effects of nitric acid decomposition. Tests should be performed over the entire range of acid concentrations that have, or can potentially contact the cheesecloth. Any alternatives to cheesecloth that are considered should be tested in this fashion as well.

3. For any cellulosic material that can be loaded with HS material, the cellulosic should be evaluated for its safe thermal capacity. If the cellulosic material is exposed to a chemical, before, during or after being loaded with HS material, the effects of that chemical on the cellulosic thermal capacity should be evaluated prior to its use.

## Conclusion

In HS processing, the ignitable (D001) or reactive (D003) properties of any cellulosic waste generated will be dependent upon the nitric acid concentration/process solution in which it comes into contact. The concentrations of nitric acid available in this process range from dilute 0.1 M, which is used for rinsing equipment and initial solution dilution, up to 15.6 M which is used for HS dissolution. Measurable nitration is possible when cellulosic material is exposed to 15.6 M acid [13], but the maximum nitrogen content capable of being produced at this concentration would not be expected to cause the cellulosic waste to exhibit unstable behavior or warrant management as a RCRA reactive waste D003. Waste cellulosic material that has contacted nitric acid at concentrations of 12 M or less should have no detectable nitration based upon the results of prior studies/testing cited [2].

The effect of nitric acid chemical decomposition on cellulosic material waste characteristics is less certain, especially for acid concentrations at 12 M and above [2]. The characteristic of thermal stability has been shown to be reduced and the characteristic of ignitability has been shown to be increased from that of cellulosic not exposed to concentrated nitric acid. Exposure time, temperature of exposure and duration of exposure seem to influence the change in these characteristics. Further testing may be appropriate to achieve a deeper understanding of these influences.

Consistent with Operating Experience Level 3 (OE3) [14, 17] guidance, cellulosic waste that has come into contact with nitric acid should be managed as a D001 waste until an OE-3: 2016-05 recommended testing technique demonstrates that the waste does not exhibit ignitable or reactive characteristics. In the HS material processing operations, examples could include spills of concentrated nitric acids used for dissolution, and wastes containing dissolved HS material solutions that have not yet proceeded past the precipitation phase.

Cellulosic material that has contacted nitric acid at concentrations less than 10 M nitric acid [15, 16], or HS material solutions where the HS material is no longer a nitrate, would no longer meet the definition of an oxidizer and require assignment of the RCRA code D001, ignitability. In HS material processing, this includes the precipitate solution after oxalic acid addition and the clad decontamination solution. The precipitate solution is less than 2 M nitric acid and the HS material is an oxalate complex. The decontamination solution is approximately 3.5 M nitric acid.

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