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# 1 Abstract

The United States Department of Energy, Manual, M441.1-1, Nuclear Material Packaging, provides detailed packaging requirements for protecting workers from exposure to nuclear materials stored outside of an approved engineered contamination barrier. The SAVY-4000 Series nuclear material packaging system is a DOE Manual 441.1-1 compliant storage system used at Los Alamos National Laboratory and across the DOE complex as the primary storage system for plutonium-containing materials. The Container Safety and Engineering Team at LANL considers internal packaging configurations as part of the safety system. Since 2015, the need to replace the suspended polyvinylchloride, or (sPVC), bag-out-bags has been made apparent, since these bags break down due to radiolysis. When the bag material deteriorates, it produces a corrosive gas known as HCl or hydrogen chloride gas and leaves behind the suspended plasticizer. The chlorine ions from HCl readily attacks the thin film passivation layer of the 316L stainless steel that makes up the SAVY-4000 nuclear material storage container's inner surface. Over the course of SAVY-4000 container surveillance operations, corrosion has been observed. While the SAVY-4000 container is continuing to perform its role robustly, the need for sPVC replacement remains a strategic goal. In 2018, a new polymer type was selected, and the first aromatic polyurethane ether, or (APU-e) bag-out-bag was manufactured by LANL. This bag did not have a filter installed and was formed by heat sealing the edges of the material together. This manufacturing method worked well for the first prototype test. APU-ether material does not produce any halogens as it breaks down over time. This means no chlorides, fluorides, etc., and no HCl gas generation. In 2022, the first real word aging experiments are coming out of the storage location for inspection and data collection. These experiments will continue until LANL is confident.

# 2 Introduction

Aromatic polyether urethane (APU-E) is a unique material that possesses good radiation stability and does not contain any halogens that are incompatible with outer stainless steel container packages. Subsequently, APU-E is an excellent candidate bag-out bag material for nuclear material storage. The current material in use, suspended polyvinylchloride (sPVC), suffers from comparatively worse radiation tolerance, and has exhibited the release of chlorine compounds as it degrades in the harsh storage environment. Testing and performance of a range of candidate materials in recent years resulted in the down-selection of fire retardant (FR) APU-E for production [1,2].

In fiscal year 2019 (FY19), commercial production of the new bag-out-bags began with NFT Inc. (Golden, CO) to produce a completed bag assembly with the new material while still passing the existing LANL procurement specification [3]. The containers used to store nuclear material are required to meet DOE guidelines to protect workers from airborne contamination, notably those outlined in DOE Manual 441.1-1. SAVY containers developed at LANL in conjunction with Nuclear Filter Technology (NFT Inc,) use a plastic bag during containerization of material and are officially recognized as "safety significant" [4]. These bag-out bags play a key role in preventing release of nuclear material to the operators during the moment of transfer (a matter of seconds) from one containment boundary (glovebox) to the next (SAVY-4000).

The current packaging configuration consists of the following: an inner container compliant with facility requirements housed inside of a polyvinyl chloride (sPVC) plastic bag-out bag, and all contained inside of a SAVY-4000 container made from corrosion resistant 316L stainless steel. This plastic bag serves to isolate the contaminated inner vessel, which stores the nuclear material, from the outer container and to prevent particulate release in case the inner container is breached. The condition of each component during the storage lifetime is periodically evaluated to ensure these materials continue to meet requirements. Engineering controls have been implemented to minimize the impact of the inner container and bag-out bag degradation that are inevitable in storage environments.

# 3 The Packaging Pilot Program

A team in the chemistry division at LANL has aged multiple materials and has conducted many process examinations. Plastic bags made from aromatic polyether urethane (APU-ether) and aromatic polyester urethane (APU-ester) were fabricated by Rich Industries Inc. and tested in the as-received condition. The thickness of these materials was measured to be 305 (+/-) 5 µm. Their chemical composition was determined by a combination of FTIR and component extraction in toluene. The average mass loss for both APU materials was measured to be only 3% of their initial weight, indicating relatively low amounts of additives, such as plasticizers. Accelerated aging experiments were performed at the Low Dose Rate Irradiation Facility (LDRIF) located at Sandia National Laboratories (Albuquerque, New Mexico). This facility uses Cs-137 sources (0.135Ci) to conduct aging studies over long periods of time. The accumulated gamma dose after 12 months of aging was approximately 180 Gy. Cs-137 sources were located at the center of custom-built aluminum carrousels with samples surrounding the gamma sources [2].

## 3.1 Phase 1: Outer Container and Specimen Selection

After initial characterization of the candidate materials, a packaging pilot program began in late November 2021. The main objective of this effort was to study the stability of the candidate APU-E materials in actual packaging configurations and storage conditions inside the facility's various storage locations. The first phase of the pilot program involved nuclear material and container selection to capture conversative conditions that polymers experience in storage. All outer containers in this experiment were SAVY-4000s. Packaging configurations were kept as similar as possible for all materials to eliminate variability between each assembly. Among those variations planned for the pilot program, outer container sizes were varied to provide the broadest sampling of storage conditions to model the actual conditions of the storage environment in the plutonium facility. Three of the outer containers chosen were 3 Qt SAVY-4000s, two were 1 Qt SAVY-4000s, and one was an 8 Qt SAVY-4000.

Select material combinations were transferred from gloveboxes into APU bags and finally housed in a SAVY-4000 container for storage testing. Information on the governing procedures for this work evolution (process) are detailed in [5-13]. APU-E, APU-E FR, and sPVC specimens were sectioned by destroying a new bag-out bag assembly. Dimensions of the specimens were approximately 3.75" long and 1.25" wide as required for mechanical testing. Figure 1 provides an overview of the loading configuration of the three polymer pieces in a 5 Qt and 8 Qt SAVY-4000. Due to the limited space in containers less than 8 Qt in volume, polymer sections overlapped. However, these were positioned to minimize overlap as much as possible. A bagged out nuclear material and inner container was then loaded on top of the candidate bag-out bag materials. In total, 6 assemblies were produced in phase 1: one control comprised of a bag-out-bag made from the current sPVC bag material, and the remaining five items bagged-out with the APU-E FR. This was done so that any signs of corrosion in or on the package observed from the APU-E FR bagged-out items can be compared to the sPVC bagged-out item. These assemblies were placed in storage for one year. Only 5 of the 6 items have been retrieved and observed thus far pending facility radiolocation work specific permits development and implementation.

*Figure 1- Placement of material samples in the SAVY container of various sizes*

## 3.2 Phase 1: Nuclear Material Selection

The bag-out bag material must be challenged by a combination of thermal energy (wattage), radioactivity, and environment chemistry. A representative sampling of the most challenging materials to store was used in this pilot study to capture the degradation of APU-E candidates more fully. Wattages and total nuclear material gram amount were kept similar for all materials to ensure more fair comparisons across the different packaging configurations.

Figure 2 shows an item that was packaged in a 5 QT Hagan outer container and an inner container 500ml conflat. Notably, the material, referred to as “Hatch” material, has an interesting mix of very small amounts of Pu-238 with other compounds and challenges the bag-out-bag as well as the internal surfaces of the approved outer container. Prior years of container surveillance have observed different “Hatch” materials with darkened and degraded bag-out-bags. This specific item was selected for this reason and for the fact that the outer container was of smaller volume. The reason why volume is important to this experiment is that if a smaller surface area of 316L stainless steel is exposed the less HCL gas will react with the surface, forcing a large quantity to flow through the lid filter media. This also results in a larger concentration of HCL gas accumulating over time inside the headspace of the container, but conditions partnered together create and maintain a challenging environment for the APU-E FR bag-out-bag material that is under investigation.

*Figure 2 - (left) "Hatch" material contained in a conflat package bagged out in a sPVC bag. (right) Residue and corrosion on the interior walls of the outer 5 Qt Hagan container.*

Figure 3 shows a quarter-quart taped slip lid inner container with a rather large amount of sPVC bag-out-bag material held up within the taped "pigtail" seal. This indicates that an appropriately sized bag-out port was not available for use during the original bag-out operation. The internal surfaces of the SAVY-4000 container display large amounts of general corrosion and some small amount of liquid PVC plasticizers in the bottom of the container. These observations are good indications that the material is challenging the bag-out-bag and was selected for the pilot study.

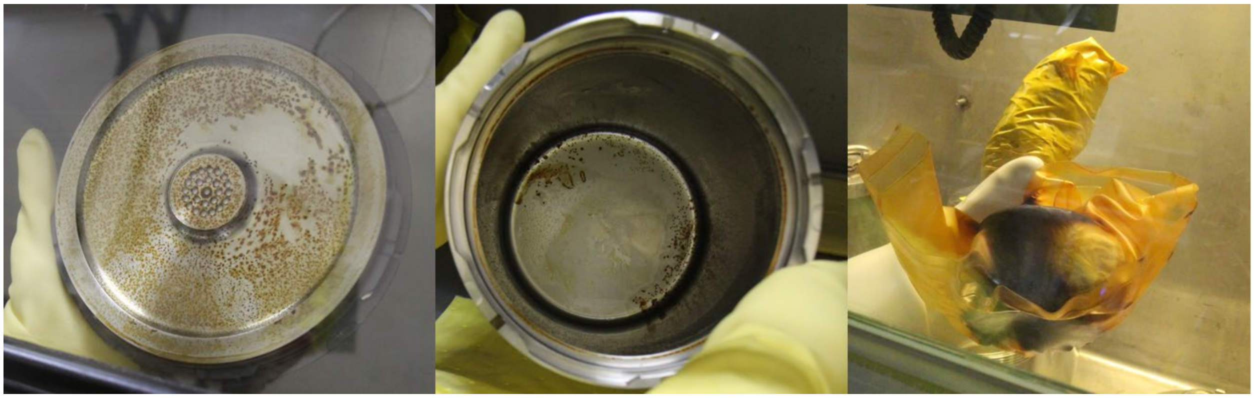

*Figure 3 - SAVY container packing configuration content verification*

Materials in the oxide form tend to have the ability to disperse within the inner container more easily than other material forms such as metals. Every small crevice that the oxide can work into, it will, making it a challenge to not only the inner container, but also the bag-out-bag. In the case of this specific item, the inner quarter quart slip lid was bagged out twice: first with a polyethylene bag, and then into a sPVC bag. This double bag technique is often employed when the primary bag is becoming too weak to handle, or there is a possible contamination concern. A new quarter quart taped slip lid is seen (far right) of Figure 4 below.

*Figure 4 - (left) ¼ Qt inner slip lid, (middle) bag condition and content verification, (right) new taped slip lid after repackaging.*

Outer containers loaded with MSE salt have historically shown a tendency to corrode in storage. In the case of this pilot program, 3 containers were loaded with MSE salt materials. These observations have driven what is commonly referred to as over-packing as a practice in the facility. Container assemblies with MSE salt material stored are placed inside the next largest SAVY-4000 container and transported to an open front hood for examination. This provides an additional barrier to release of nuclear material and ensures the safety of the workers during handling and transportation of the container.

This practice is especially important for these material types contained with Hagan containers. Figure 5 provides an example of this assembly. Corrosion of the stainless-steel components near the filter show that the headspace of the container was rich with corrosive species. However, this Hagan container could not be opened by operators due to corrosion of the outer threads (locking mechanism). Such a state indicates that the Hagan was not properly closed to prevent the release of corrosive gasses through the primary seal of the container. Retrieval of the nuclear material required operators to introduce the entire assembly into a glovebox and cut open the lid of the 5 Qt Hagan container. Further investigation found that the nuclear material oxidized and began expanding inside the inner container. This caused the inner slid lid container to open slightly, exposing the sPVC bag-out bag directly to the nuclear material and causing rapid degradation. LANL's AMPP-4 Science and Engineering team conducted further data collection into the corrosion behavior on the outer Hagan container [3].

*Figure 5 - Hagan container with corroded threads and corrosion on the interior surfaces. Inner packaging with degraded bag-out bag and slip lid container are also shown.*

Figure 6 provides an overview of the different parts of the container package to host the first item to ever be bagged-out in any form of APU-E performed in FY18. The bag in this case was manufactured by LANL personnel and heat sealed. The bag did not have a filter installed at the time of packaging. The slip lid on the far right in Fig.6 was pristine at the time of packaging in

FY18. Images indicate that general corrosion progressed throughout the inner container. The internal surfaces of the outer 3 Qt SAVY-4000 that this item was placed into show no visual signs of corrosion, as seen in the far left in Fig. 6. It was speculated that no corrosion was observed because the bag-out-bag did not have a filter installed, so no corrosive gasses produced from the MSE salt itself could interact with the 316L stainless steel body wall of the three-quart SAVY-4000 container. This item was bagged-out with a sPVC bag as the control for Phase 1 of the pilot program. The storage performance of the original APU-E material will be compared to the same container assembly with an sPVC bag-out bag after one year in storage to determine the extent of corrosion resulting from bag-out bag degradation. Moreover, any differences observed with the new bag-out bag candidate (APU-E FR) could also be compared to the performance of the first APU-E bag-out bag material shown in Fig. 6 below [14].

*Figure 6 - From left to right: Interior pictures of the outer 3 Qt SAVY-4000, APU-E bag-out bag, slip lid inner container, lid of the inner container exhibiting general corrosion.*

Figure 7 provides images of the last material selected for Phase 1 experimentation. This item was the largest physical item of the experiment (largest total gram amount). This item also was the most radioactive with 2R/hr beta-gamma and 25.1 neutron/hr. Due to the higher dose rates, handling of this item during the repacking was kept to a minimum. The sPVC bag seen in Figure 7 below is heavily degraded, a sure sign that nuclear material decay products are breaking down the bag-out bag. The corroded tamper indicating device (TID) wire also confirms the production of corrosive gasses venting through the filter diffusion holes. This material also produces HCL gas from itself as a molten salt with a known high Americium content.

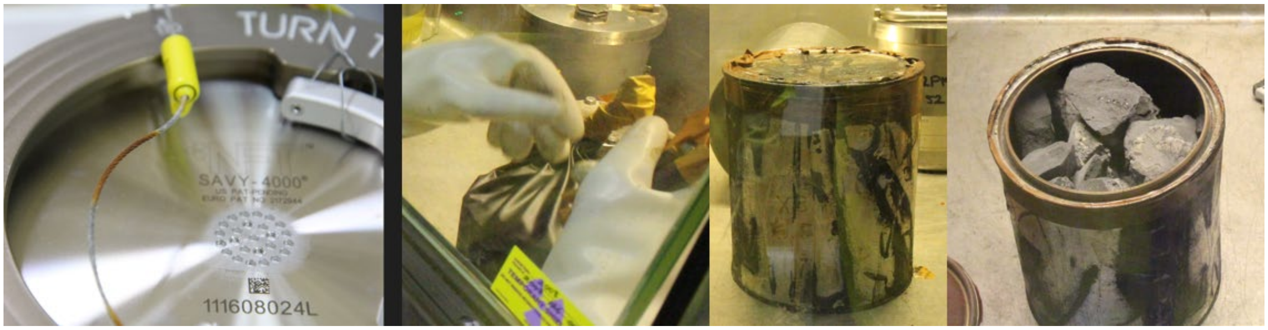

*Figure 7 - SAVY with the largest inner continue and material in the pilot program.*

This item also has the most surface area of the new APU-E FR material exposed to the internal surfaces of the new 8-quart SAVY-4000 comparatively speaking to all the other APU-E FR items.

The goal of this is to determine if internal free volume is a major contributing variable to the corrosion growth rate problem inside SAVY-4000 containers in general. The theory is if there is more bag-out-bag material for nuclear or HCL gas to interact with, there should be more corrosion growth. This item will be able to provide the data needed to analyze this theory.

*Figure 8 - Glovebox fissile material handlers conducting bag-outs of the APU-e items.*

With the assistance of LANL's AMPP-4 Science and Engineering team, the bag-out effort completed over a two-month-long period starting in November 30, 2021 and ending December 1, 2021. All six items were repacked in new inner containers ranging in volume from ¼ quart slip lid, 1 Qt slip lids, and a single 6 Qt slip lid for the largest item. All required non-destructive analysis measurements were collected and new dose measurements performed. The items were then shelved in the TA-55 vault within several weeks of each other. This timeline is critical to maintain the exposure time of the bag-out-bag to the nuclear material.

# 4 Ongoing and Future Efforts

Phase II began in FY 23 and involved the mechanical and chemical characterization of small APU-E, APU-E FR, and sPVC samples subjected to storage conditions for one year. Unpacking of the first three of six containers took place in November-December 2022. Visual inspections were employed to locate any signs of corrosion to the inner surfaces of the SAVY-4000 container. Analysis of the first APU-E bag-out bag used for a container assembly in FY18 was removed by operators during the repackaging work and the material was sent to MST-16 for further analysis. This work is ongoing in FY23, and results are still be collected at this time [1,2].

As part of the bag-out bag replacement program, a team in LANL's C-CDE group will assist with a series of tests that will be implemented to ensure quality of the new APU (ether) bags. These measures would help minimize batch-to-batch variation and are based on the characterization work described in this report. The proposed quality control experiments by chemistry division are outlined in the list that follows. Characterization methods APU(ether) Error (±) Comments: Thermal DSC (oC) -42 / 68 5 Glass Transition TGA (oC) 310 10 Onset degradation, Mechanical Tensile Strength (MPa) 57 5, Tension test Elongation at break (ASTM D412) (%) 570 20, Maximum Load (N) 170 20, Puncture test, (ASTM D4833), Surface Contact Angle (o) 103 5 Hydrophobicity, Chemical FTIR peak (cm-1), All peaks should be present: 3312 (-NH stretching), 1718 (C=O stretching), 1687, amide I (C=O), 1537, 1593 (aromatic C=Cstretching). [1],[2]

The characterization planned for pristine bags as a quality control measured are also underway for the exposed APU-E candidate and sPVC sectioned samples loaded in storage containers. Retrieval of nearly all items has completed with several of the tests yielding preliminary results. Mechanical testing was delayed due to a test design change. The APU-E and sPVC specimens subject to storage conditions were cut in half, with one portion repacked with the material and placed back in storage and the other portion removed for testing. Due to the smaller specimen size, punch dies for the tensile test were redesigned and fabricated to accommodate the smaller amount of material. Results from mechanical testing are expected by the end of April 2023.

# 5 Conclusions

The accelerated ageing studies conducted by chemistry identified two polyurethane plastic bags as replacement candidates to currently used sPVC bag-out bag, which show signs of degradation over its lifetime (loss of plasticizer, radiolysis and dehydrochlorination). The two materials evaluated in the present work were aromatic polyether urethane and aromatic polyester urethane. These materials were accelerated aged under unique conditions that combined gamma radiation and thermal treatments simultaneously. Aged samples were characterized by a large set of experimental techniques to gauge changes in structure-property relationships. Characterization by FT-IR showed no significant changes in chemistry, but evaluation of gases in the headspace confirmed oxidative degradation of both APUs due to aging. Thermal stability and hydrophobic properties were little affected, whereas the mechanical behavior showed more changes with aging. The maximum tensile stress at break decreased slightly, whereas the maximum elongation increased for aged APUs compared to control samples. Furthermore, APU (ether) samples aged in SAVY containers at TA-55 showed similar changes compared to samples aged under controlled lab environment. This result helps to validate accelerated aging studies and to guide the replacement of PVC bag-out bags used in the storage of nuclear materials. Finally, APU (ether) bags were chosen over APU (ester) bags because of excellent performance as demonstrated by aging studies performed under realistic conditions and cold bag out exercise conducted at TA-55.[1],[2].

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