

LA-UR-23-24351

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Intended for: Institute for Nuclear Materials Management (INMM) Annual Meeting, 2023-05-22/2023-05-26 (Vienna, Austria)

Issued: 2023-04-25



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Development of a Uniformly Hydrophobic Filter for Nuclear Material Handling and Storage

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ABSTRACT

Los Alamos National Laboratory (LANL) employs a variety of filtered containers to handle nuclear material, both inside and outside of a glovebox. A novel filter has been developed to address the unique challenges of filtered in-glovebox nuclear material handling and storage by improving current containment methods, enhancing resistance to water, heat, and alpha radiolytic degradation.

Criticality safety controls currently limit material amounts that can be handled inside a glovebox without a water-resistant container to mitigate the risk of a criticality accident posed by credible flooding accident scenarios. These limits and the current population of approved, filtered water resistant containers pose production inefficiencies due to ergonomic and radiolytic degradation concerns, requiring a robust, filtered, water-resistant container that can meet expanded safety basis and criticality requirements for in-glovebox use, while reducing confusion and ergonomic risk to workers. Creating a filter that is resistant to high temperatures and alpha radiolytic degradation, while being hydrophobic throughout its thickness, would help address the disadvantages of these other filtered containers when paired with a new ergonomic container design and would allow for a single container for multi-faceted use throughout the facility.

Novel methodologies developed by LANL have been refined by NucFil, LLC (NFT), to design a hydrophobic filter element. By improving the water pressure resistance of the filter and defining a viable production process, it has been possible to move the technology rapidly towards implementation. Through collaboration between NFT and LANL, the new filter withstands temperatures upwards of 400°C and water pressures up to 72" of water column (17.92 kPa) with less than 50 mL of water entry. Additionally, at a test flow rate of 200 standard cc/minute (SCCM), the filter can maintain an efficiency rating of at least 99.97% with a pressure drop of less than 4" of water column (about 1 kPa) across the filter. The developmental techniques, methodologies, and production process will be presented, along with the filter's characteristics, performance, applications, and future expanded use potential.

Introduction

Currently, Los Alamos National Laboratory (LANL) utilizes a variety of different containers, including the SAVY-4000, for storage needs within their gloveboxes. The SAVY-4000 is an interim storage container primarily designed for use outside of an engineered control barrier (e.g., a glovebox), but because of its robust design and water-resistant capability, is approved for use inside of a glovebox at the LANL plutonium facility. The filter in the SAVY-4000 is comprised of ceramic filter discs and a single water-resistant polytetrafluoroethylene (PTFE) membrane. Accelerated aging test results have suggested that the hydrophobicity of the PTFE membrane degrades under

alpha radiation exposure (only found inside of a glovebox environment) over the 15-year life of the SAVY-4000 container. While this degradation is well characterized and acceptable within LANL's specifications, with continued use inside of gloveboxes at LANL and the desire to extend the SAVY-4000 lifetime to 40 years, any indication of degradation is a cause for seeking an improved solution to replace the SAVY-4000 in this application. To achieve this, LANL developed a fully hydrophobic filter, using the same base ceramic media as the SAVY-4000 filter, that would better withstand direct exposure to alpha irradiation and provide additional defense against elevated temperatures.[1]

Once the preliminary filter design was finalized, LANL and NFT began development of container systems into which the filter would be implemented. Originally, the filter was designed for a water ingress testing pressure specification of 6 inches of water column (6" W.C., or ~1.5 kPa) but was changed by LANL to 72" W.C. (~18 kPa). The criticality safety scenario assumes that the entire container is submerged under water such that the top surface of the lid is at the specified distance from the top surface of the water. Due to this change, LANL's original filter design was no longer feasible because at higher pressures, the unbonded fibers could move freely, allowing water to enter the container. Therefore, NFT built upon LANL's initial work to develop the hydrophobic degradation resistant aluminosilicate (HyDRA) filter that could contend with these higher pressures.

Preliminary Work

Prior to the water ingress specification change, NFT began efforts to scale up the methods developed by LANL to meet production-level demands. LANL's method indicated that discs or sheets of unbonded aluminosilicate fiber were to be immersed in solution before being moved into a furnace for heat treatment. While this process worked well for small batches, the fragility of the fiber media when saturated (see Figure 1) made it difficult to handle in large batches. Even when dry, it tore easily, prompting concerns about scrap rates during filter installation. NFT subsequently prioritized enhancing the filter's durability as the first step in improving the scalability of the initial process.



Figure 1: Image of a sheet of saturated fiber that was ripped during handling.

With the NucFil[®] filter line as a staple of NFT's business, NFT has long employed a robust process for manufacturing carbon filters via vacuum slurry molding. It was determined that this molding process could be similarly implemented for the new ceramic filters. Sheets of aluminosilicate were mixed into a slurry paste and then molded into the desired filter shape. This method, seen in Figure 2, produced thicker, denser filters that were more suitable for production than the initial thin discs. It was during this development stage that LANL proposed the increase in water ingress pressure from

6" W.C. (~1.5 kPa) to 72" W.C. (~18 kPa). Testing showed that the new molded filters, though hydrophobic, were unable to withstand the increased ingress pressure because the unbonded fibers could be moved aside freely which allowed water to pass through into the container. NFT then focused on increasing the filter's rigidity by researching potential bonding agents to introduce into the matrix.



Figure 2: Images of the fiber slurry (a) and the molded, unbonded filters (b).

After testing various bonding agents, a phenolic resin was selected to construct a matrix that would hold the fibers in place. Its specific chemical properties suggested that it would not impede the formation of a hydrophobic layer on the fiber surface. The selected resin is also used extensively in NFT's carbon filter manufacturing process and could therefore be smoothly implemented into the ceramic filter process. Preliminary results, seen in Figure 3 below, showed that an additional post-cure carbonization step prior to creating the hydrophobic layer led to a robust, hydrophobic filter that could withstand the 72" W.C. (~18 kPa) requirement. With steps towards a viable production-type filter, NFT's development transitioned to improving the repeatability of filter manufacturing.



Figure 3: Images of the pre-cure molded filters (a) and the carbonized, hydrophobic filters (b).

Process Development

The introduction of phenolic resin into the aluminosilicate fiber matrix greatly improved the rigidity of the filters, allowing them to withstand 72" W.C. (~18 kPa). Additional testing, however, revealed that repeatability would be an impediment to further development. To surmount this obstacle, NFT devoted time to better understanding the chemistry and critical characteristics behind the formation

of the hydrophobic coating. The substance chosen by LANL was perfluorodecyltrichlorosilane (PFOTS) which forms a hydrophobic self-assembled monolayer (SAM) by bonding to hydroxyl groups on the aluminosilicate fibers. The long, fluorinated tail group that is created is common for hydrophobic applications. The chemical structures and formation of the SAM are shown in Figure 4 below.

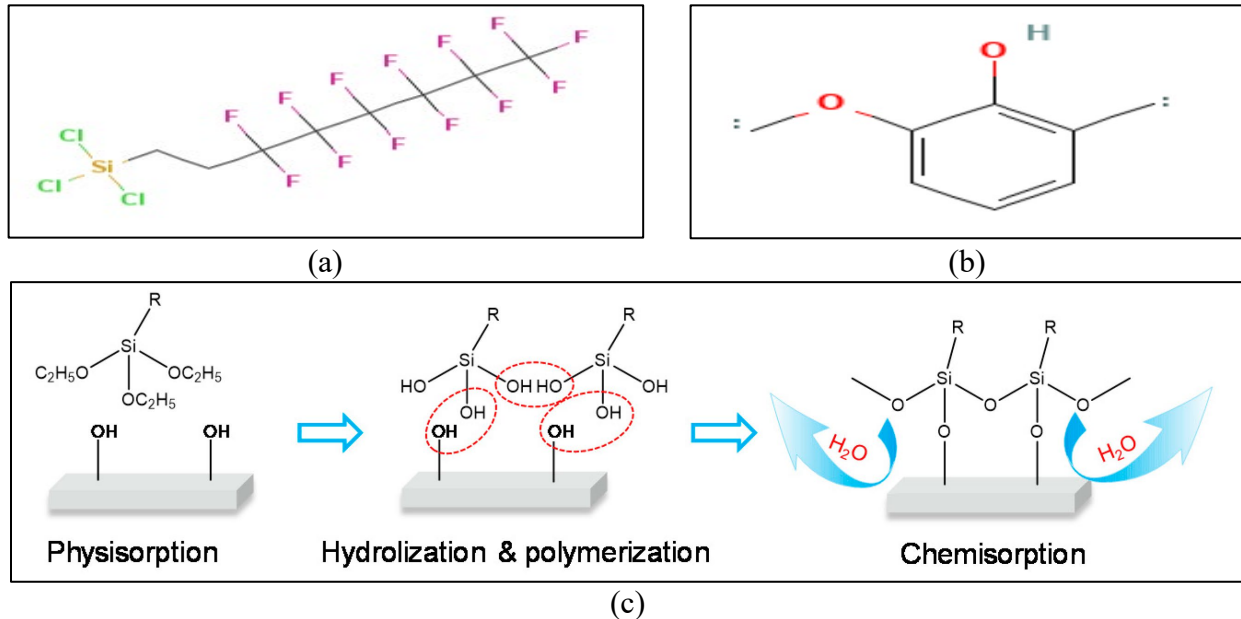


Figure 4: Images of the chemical structure of PFOTS (a), the chemical structure of phenolic resin (b), and a generalized mechanism for SAM formation (c).[2]–[4]

The preliminary testing had suggested that partial carbonization of the phenolic resin would strengthen the matrix without significantly obstructing the aluminosilicate bonding sites, as the resin also contains potential PFOTS bonding sites. However, additional research revealed that as the phenolic resin progresses through carbonization, the potential bonding sites are driven off, and the result is a largely hydrophilic matrix. Once this was understood, NFT eliminated the carbonization step completely and focused on optimizing the strength of the phenolic resin structure in its cured form. Images of the carbonized and cured phenolic resin fiber matrices are in Figure 5 below.

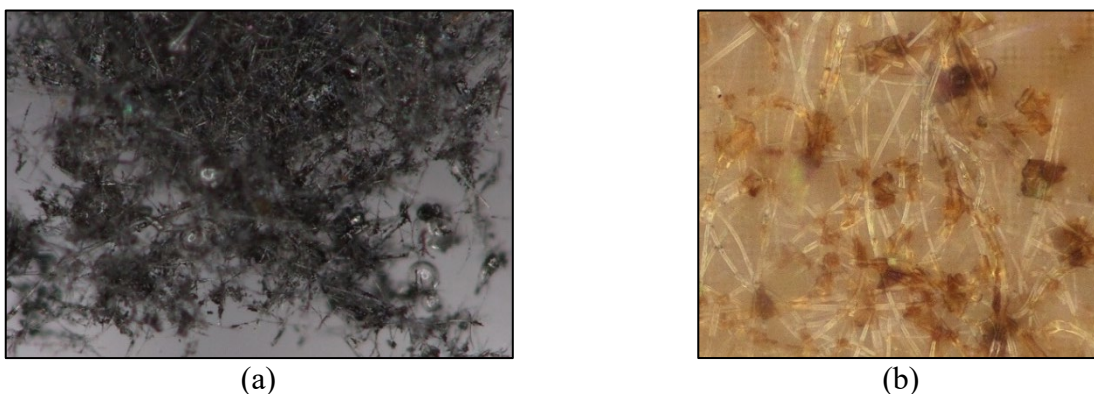


Figure 5: Images of the carbonized phenolic resin (a) and the cured phenolic resin (b) incorporated into the ceramic fiber matrix.

Before choosing to eliminate the carbonization step completely, a significant effort was put into circumventing the bonding site challenges by creating a thin layer of structural carbon on the outside of an unbonded filter. Resin solubility and application methods were explored as ways of isolating its coverage to the external surfaces of the filter. Successful methods produced the desired filter morphology and increased internal hydrophobicity. However, they were unable to withstand the 72" W.C. (~18 kPa) requirement because the phenolic layer became brittle without sufficiently compensating for the internal fiber flexibility (see Figure 6 below).

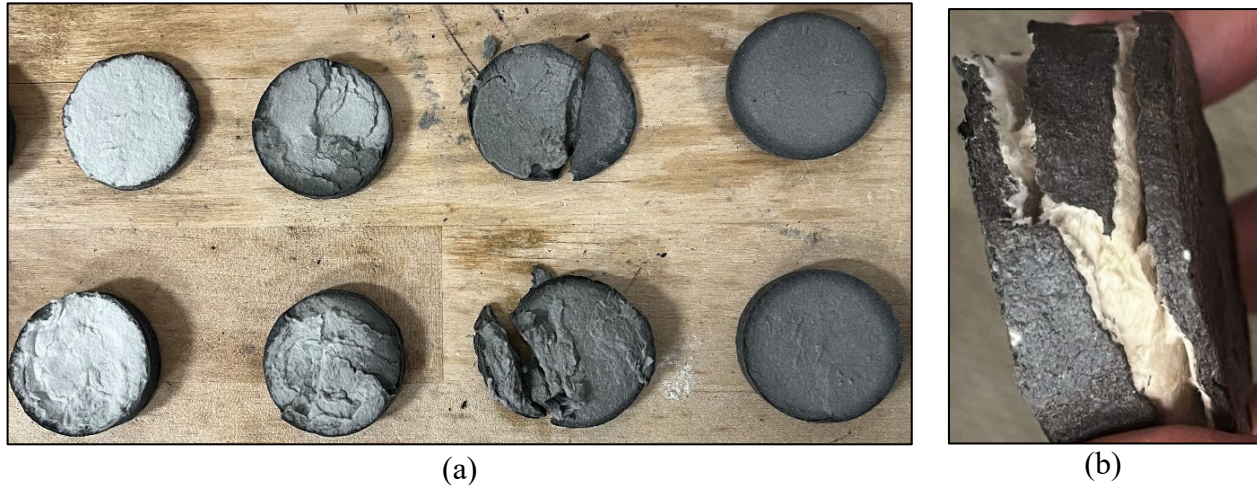


Figure 6: Images showing variations in residual carbonized phenolic from different process methods (a) and the brittle nature of the externally coated filters (b).

After this method was determined to be unfeasible, NFT's focus returned to dispersing the resin throughout the fiber matrix. Various resin concentrations were explored to achieve sufficient filter rigidity with the minimum amount of resin. Once this proportion was determined, resin curing time was tested (see Figure 7 below) and established as having a negligible impact on hydrophobicity. Therefore, the curing time was selected for the minimum time required for resin crosslinking to generate sufficient filter strength.



Figure 7: Images showing the results of different resin curing times with the selected curing time highlighted in black.

The testing up until this phase had cumulatively provided critical insight into the mechanisms driving the formation of the hydrophobic layer. While PFOTS initially reacts readily with the aluminosilicate surface, the bonding step slows as bonding sites gradually become unavailable. Additionally, the dense, porous fiber matrix requires a unique approach to surface silanization because the available surface area is extremely large. Full monolayer assembly can take hours or

even days with smaller surface areas, so examining ways to promote and accelerate bonding on the fibers was critical. Therefore, NFT developed a process for enabling maximal bonding with production feasibility in mind. A significant advancement came with the encapsulation of the heat treatment step utilizing a tube furnace. It is hypothesized that enclosing the solution-soaked filters under conditions where the PFOTS had increased mobility promoted monolayer packing, leading to drastic improvements in the reproducibility of the hydrophobic coating (see Figure 8 below).

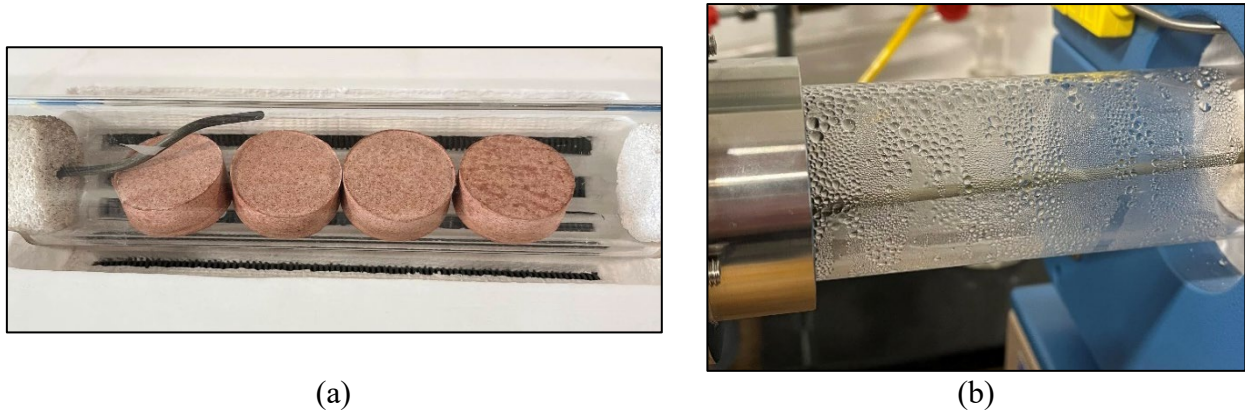


Figure 8: Images showing the encapsulation heat treatment (a) and resulting condensation (b).

The structural stability of the SAM is driven in part by Van der Waals interactions between the fluorinated tails on the PFOTS molecules. Defects in the uniform molecular ordering can arise from factors such as surface or airborne impurities. In NFT's initial attempts at enclosed heat treatment, enough condensed liquid was produced to re-soak the filters. This posed problems for the formation of the SAM, as solvent impurities were inhibitive of proper ordering, leading to a significant reduction in hydrophobic performance. The ordering mechanism is illustrated in Figure 9 below. A simple change in placing the filters above the bottom of the quartz tube during the heat treatment mitigated this issue and was the final major step to achieving extremely consistent hydrophobic filters.

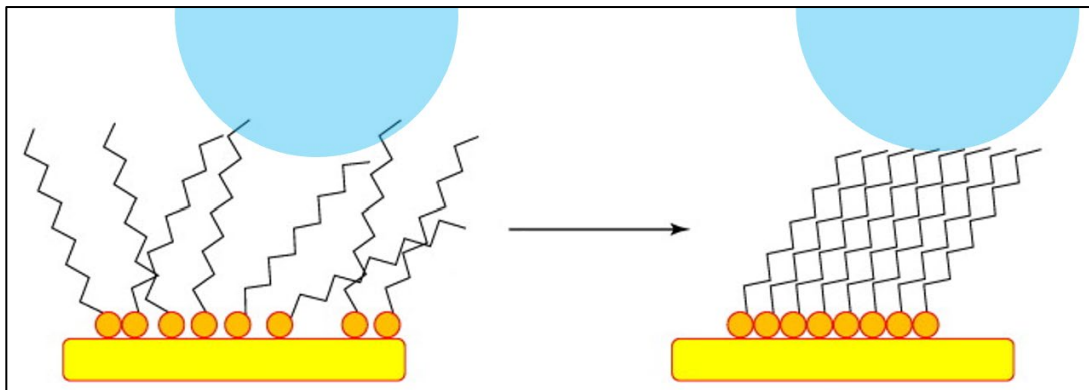


Figure 9: Diagram showing the mechanism of SAM ordering.[5]

Container Design

With the filter fully developed, it could be implemented into two new designs: the In-Glovebox container and the SAVY-5000 container. Both designs are built for radiological work within the

LANL facility, but their different functions necessitate different specifications. The two major differences in the specifications that drove variations in container geometry are shown in Table 1 below.

Table 1: In-Glovebox & SAVY-5000 Requirements

Container Type	Container Function	Water Ingress Requirement	Differential Pressure Requirement
In-Glovebox	Handling and storage of nuclear material inside of a glovebox	<50 mL ingress after 2 hours at 72" W.C. (~18 kPa)	<4" W.C. (1 kPa)
SAVY-5000	Interim storage of nuclear material outside of an engineered control barrier (e.g., a glovebox)	<50 mL ingress after 2 hours at 6" W.C. (~1.5 kPa)	<1" W.C. (0.25 kPa)

Since the water ingress requirement for the In-Glovebox container is significantly higher, its filter requires much greater compression to restrict fiber movement and minimize porous areas where water could infiltrate. The compression was optimized by testing at small intervals, as it became clear that small increases in compression lead to profound increases in differential pressure. An amount of compression was selected that satisfied both the water ingress requirement and differential pressure requirement for the In-Glovebox container. To further impede water infiltration, a knife edge was added to the filter cavity, and a round protrusion was added to the filter cap. These features create a tortuous path for the water and resulted in drastically decreased water ingress into the container. Due to this success, the knife edge design was also implemented into the SAVY-5000. However, with the less stringent water ingress requirements for the SAVY-5000, a filter cup design was utilized for less filter compression than the filter cap. The differences in the In-Glovebox and SAVY-5000 containers are outlined in Figure 10 below.

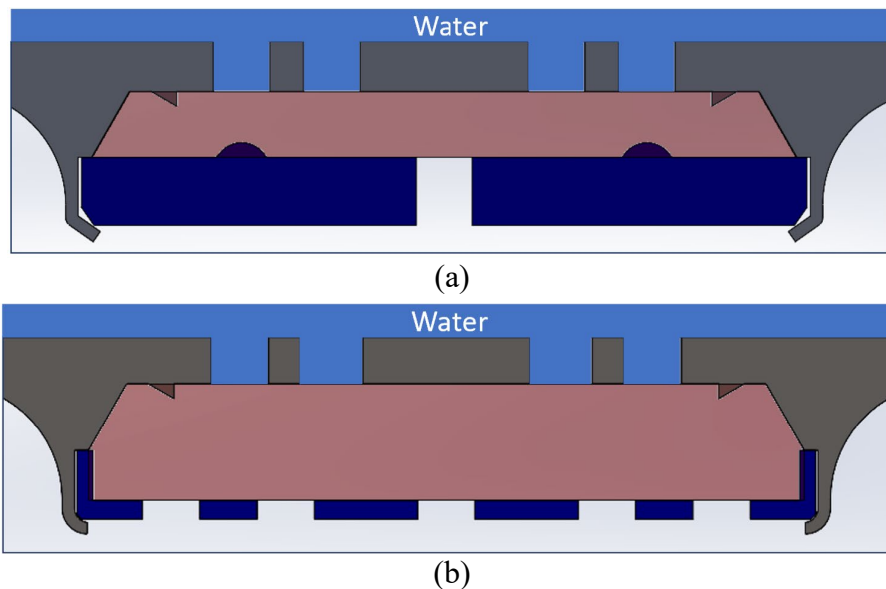


Figure 10: Images detailing the filter geometry for the In-Glovebox (a) and the SAVY-5000 (b) containers. Note that the lid is depicted in gray, the filter in red, and the filter cap in dark blue.

Characterization

With an established process for manufacturing passing filters, NFT sought to juxtapose successful and unsuccessful filters through a variety of characterization methods. Contact angle measurement, Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), energy-dispersive x-ray spectroscopy (EDS), and x-ray fluorescence (XRF) were each attempted. The objective for each spectroscopy method was to detect fluorine, as this would be indicative of the presence of PFOTS.

Contact angle measurement is performed by determining the angle between the surface and a small water droplet. This angle quantifies the surface as hydrophobic when the angle is greater than 90° . [6] Contact angle measurements were taken throughout testing, but they were not indicative of passing or failing filters because many of the failing filters were still hydrophobic. Additionally, due to nonuniformity of the filter surface, it is difficult to accurately determine the location where the droplet meets the surface, subjecting the measurements to a significant potential for error. However, it can be concluded that the final production method produces filters with contact angle measurements upwards of 130° . Images of two contact angle measurements are in Figure 11 below.

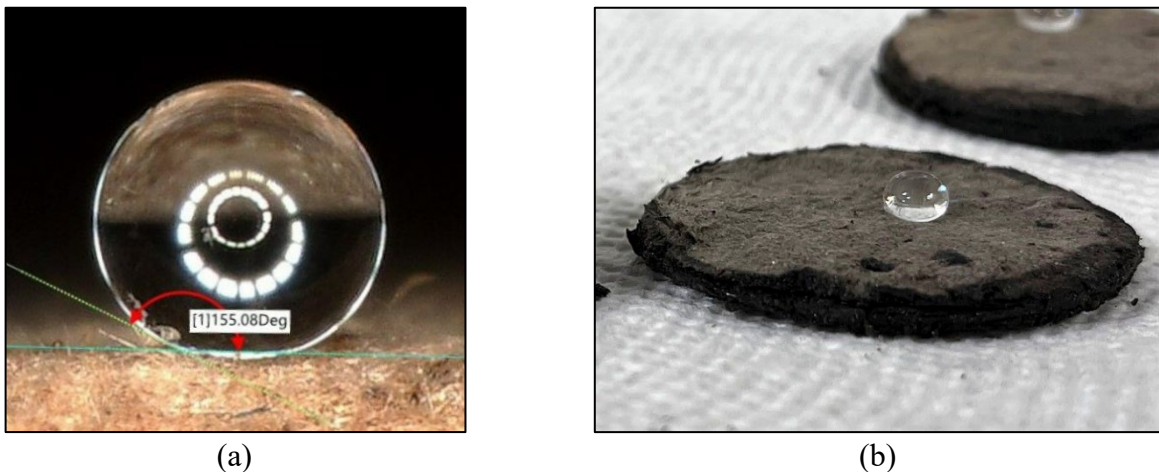


Figure 11: Images showing a contact angle measurement for a final HyDRA filter (a) and a droplet of water on a carbonized filter (b).

The results from FTIR, while largely inconclusive, were able to offer some insight into the chemical composition of the filter (see Figure 12). In Figure 12a, the peaks around 3450 cm^{-1} could be signatures of several different functional groups including the $-\text{OH}$ groups on the aluminosilicate. [7] The slight decrease in the peak noted for the PFOTS-treated fiber may show a decrease in $-\text{OH}$ groups due to the PFOTS bonding to those sites. The significant increase noted for the PFOTS- and kiln-treated fiber are suggestive of phenol which has a strong peak around 3340 cm^{-1} . [8] This would make sense because the kiln used to treat the filters is used heavily in NFT's phenolic resin-containing processes and likely would deposit an appreciable residue onto any filters heated within. The major difficulty with this characterization is outlined in Figure 12b, as the fluorine signature peak overlaps almost entirely with the silica signature peak. There is a very small increase in the peak location for the PFOTS-treated fibers, suggesting a move towards the fluorine peak. Finally, the area under these two peaks increases to a moderate degree, further suggesting an overlapping peak closer to fluorine's signature.

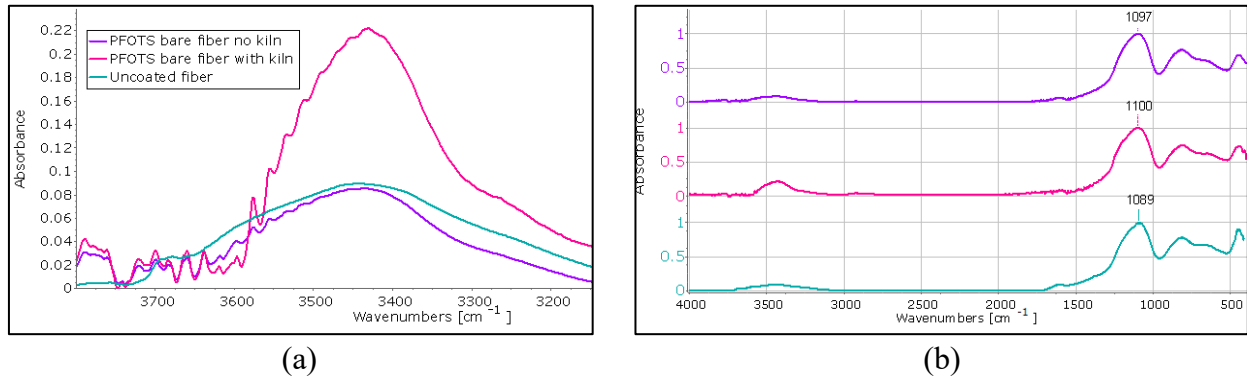


Figure 12: Images displaying a region in the FTIR spectrum indicating the presence of phenolic resin (a) and a region proposed as an indication of PFOTS (b).

However, due in part to the ultra-thin nature of the PFOTS coating, none of the spectroscopy methods outlined above were able to detect an appreciable amount of fluorine. Furthermore, EDS proved unsuccessful because the insulating nature of the aluminosilicate caused the electrons used for testing to charge the sample and distort the measurement (see Figure 13 below), making it impossible to collect data without some type of charge-dispersive setup. Therefore, NFT plans on continuing attempts to characterize the HyDRA filter. X-ray photoelectron spectroscopy (XPS) was highlighted as a common method for measuring similar coatings but was unavailable at the time of testing and will be reexamined for future characterization attempts.

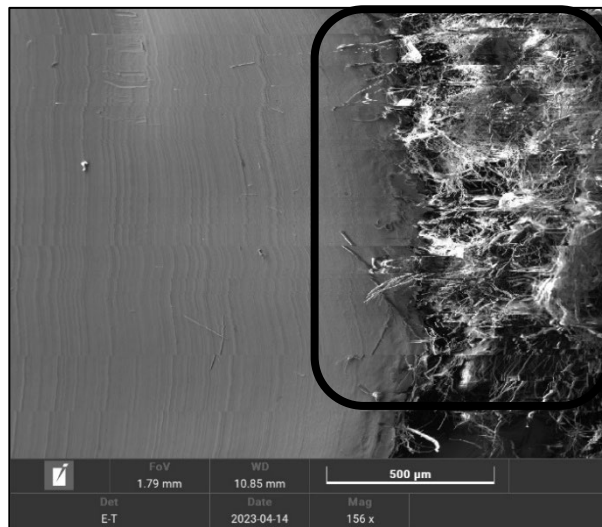


Figure 13: Image distortion, highlighted in black, seen during EDS from the sample charging.

Conclusions

Building on LANL’s process for producing a hydrophobic filter coating, NFT was able to generate a robust hydrophobic filter that is ready for production-scale manufacturing. Introducing a slurry molding process and a phenolic resin binder enabled NFT to greatly improve the robustness of the filter so that it successfully met the 72" W.C. (~18 kPa) water ingress pressure requirement. See Figure 14 below for the differences between LANL’s filter and the HyDRA filter. A thorough understanding of the PFOTS bonding mechanisms and critical processing characteristics facilitated

progress towards a well-ordered hydrophobic coating. Finally, optimizing the geometry of the In-Glovebox and SAVY-5000 containers for their respective specifications proved the feasibility of the HyDRA filter for multiple applications. NFT will continue to investigate characterization methods to determine definitive qualities between passing and failing filters. Additionally, NFT will continue developing processes and designs for the implementation of the HyDRA filter media into its NucFil[®] product lines. Overall, with its ability to withstand high water ingress pressures, radiation, and other forms of degradation, the HyDRA filter has the potential to improve the health and safety of workers within the nuclear industry and beyond.



Figure 14: Images displaying the HyDRA (a) and LANL's (b) filters.

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