LA-UR-16-28605

Hydrophobic Filter Material for Nuclear Material Transportation and Storage Containers - 17518

Kirk Reeves, Tristan Karns, Brian L. Scott, Laura E. Wolfsberg, Paul H. Smith

Los Alamos National Laboratory

P.O. Box 1663, MS E551, Los Alamos, NM 87545

Abstract

Los Alamos National Laboratory has begun development of hydrophobic or super-hydrophobic inorganic filter materials that resist water ingress after exposure to radiation and/or elevated temperature. Filters that are currently available depend on carbon composites and/or organic polymers for their water resistant/hydrophobic properties to minimize water ingress. However, facility and transportation accident scenarios often include fire, impact and subsequent water spray or flooding conditions. A purely inorganic hydrophobic filter material could have enhanced resistance to fire and radiation damage, and continue to minimize water ingress after such an accident. Such filters could broaden the use of filtered containers in the transportation and storage of nuclear materials, and could have broader implications in other industrial applications. The goal is to create a porous inorganic material with hydrophobic properties that maintains or exceeds the current performance criteria for particulate filtration efficiency, pressure differential, air flow and hydrogen diffusion. The materials developed in this project show promise in evaluations for use as enhancements to the SAVY 4000 nuclear storage container that is becoming widely used around the DOE complex. Preliminary results indicate that the treated filters provide resistance to a water column pressure test and have filtration efficiencies and air flow pressure drops that meet the current performance criteria. There are various treatment options being tested to help determine the best path forward.

Introduction

The current SAVY 4000 nuclear material storage container utilizes a polytetrafluoroethylene (PTFE) membrane to achieve a water-resistant filter seal. This membrane will likely become degraded in the event of a fire and the container will no longer be water-resistant. The PTFE membrane will also degrade with exposure to radiation, which is becoming more important because the containers are currently used in gloveboxes. A purely inorganic hydrophobic filter material would have an enhanced resistance to fire and radiation damage as compared to material with organic properties. A literature study was performed to investigate various alternatives that may be available. The new hydrophobic material could be used in retro-fit fixture for containers currently in use, or in the manufacture of new containers. The current SAVY 4000 containers use a ceramic fiber filter to allow the containers to vent while preventing significant particulate release. A literature

review showed that the use of a fluorinating agent on an inorganic substrate would produce a hydrophobic material. [1] Experiments were conducted to investigate if coating the Fiberfrax filter used in the SAVY-4000 containers would produce a hydrophobic material which would maintain its filter functionality.

Experimental

Initial testing was done on copper foil and a porous copper foam. The copper foil was done prior to the foam to ensure the literature results could be duplicated. In both cases, the copper was heated to create a layer of copper oxide nanowires to form. The foil and foam was then immersed in a PFOTS solution and cured. The samples were then taken to a failure temperature. This was done in increments with test done on the hydrophobicity in between each test. With the successes found with the porous copper foam, the study then moved to the Fiberfrax being sputter coated with copper. This was done with varying thicknesses of the coating. The copper sputtered Fiberfrax filters underwent a similar array of testing as the porous copper foam and the copper foil.

The success of the testing on other materials led to testing of treating the Fiberfrax directly. The Fiberfrax material was directly immersed in the PFOTS treatment and cured. Experiments were performed with various solution strengths and curing procedures. Attenuated Total Reflectance infrared spectroscopy (ATR-IR) was used to analyze the surface chemistry of treated and un-treated samples. This was done to help determine the mechanism of the PFOTS binding to the substrate. The various solution strengths and curing procedures underwent the same tests as the previously treated samples.

The treated material was cut into disk which were the same size as the filters used in the SAVY-4000 container. The SAVY-4000 filter consists of 3 layers of Fiberfrax material. Using the thickness of the Fiberfrax and the assembled filter cup depth, the amount of compression was determined. This allowed a fixture to be made that would allow for the treated material to be compressed to the same amount as the material that is currently used. The fixture was used for both the filter efficiency, air flow pressure drop, and the water penetration tests, allowing for minimal handling of the treated material for each test.

The filtration ability of our most optimal filters was tested using an oil droplet generator with attached photometer for measurement. Filters were tested to ensure that they met LANL specifications of capturing "greater than 99.97% of 0.45 micron mean diameter dioctyl phthalate (DOP) aerosol at the rated flow (200 cm^3/min) with a DOP concentration of 65±15 micrograms per liter." [2] However, polyalphaolefin oil (POA) was used as a substitute in our oil droplet generator for this test to avoid carcinogenicity of DOP. Aerosol concentration was measured via a photometer both upstream and downstream from the filter in question. Percentage of droplet penetration, as well as pressure drop across the filter was also measured using the same system. The test system used was developed for the testing of in-use containers for surveillance of the filter performance. [3]

A water column testing apparatus was used to further determine the degree of hydrophobicity of samples, as well as to determine the maximum amount of water that the filter could hold before ingress into the container. Water was pressurized against the filter sample placed in a sealed holder similar to that of a SAVY container. Each filter was tested under pressures calculated to be similar to 6 and 12 inches of water for dwell times of up to two hours.

Results

Both copper foil and foam became hydrophobic with contact angles of 120°on average. The copper foil surface containing CuO nanowires flaked off after the oxidative heating to 550°C for 24 hours. The copper foil result established the literature technique. Copper foam did not have problems with flaking although some cracks were visible, and nanowires were apparent on most of the surfaces. Even after heating to 300°C, a copper foam sample was able to rest on the water's surface tension, whereas, an untreated copper foam piece of the same size, sank. The 63% porous copper disk was able to hold a one inch column of water 36" high for at least 1 minute. None of the copper foam samples were still hydrophobic after heating to 550°C for 2 hours even though there were copious amounts of nanowires present, suggesting that the PFOTS decomposes or combusts. The EDS spectrum shows that the Si peak was much smaller after heating, and the C peak was absent. Failure tests for copper foam materials showed a maximum failure temperature of 450°C. At this time copper materials have only received one coat of PFOTS at 1 mM concentration. The treated 63% porous copper filter supported a 1 inch diameter water column of 36 inches in height. [4]

The 1 μm Cu coating on Fiberfrax turned to a gray coating after heating to 550°C for 24 hours. The similarly treated Cu sputter-coated Fiberfrax samples of 3 μm and 50 nm were darker and lighter, respectively, when compared to the 1 μm coated sample. Because the 50 nm Cu coating was so thin, it was not cleaned with 1M HCl, whereas, the 3μm Cu coating was immersed for 1 minute in the 1M HCl. Although the surface of the 50 nm CuO coating is barely gray, nanowires can be seen throughout it. [4]

A water contact angle goniometer apparatus was used to determine contact angle and to quantify relative hydrophobicity of each sample. All treated samples showed water contact angles greater than 120°. In reality, contact angles are likely higher, but the fibrous surfaces made it difficult to measure the contact angle. With various treatment techniques, the failure temperature of the Fiberfrax to lose hydrophobicity was found to be 475°C. The contact angle and associated temperature are given in Figure 1. Aerosol testing was performed with a single layer of treated material compared to the in-use containers having 3 layers of Fiberfrax material. The testing determined that the most promising treatments

passed the current criteria for the SAVY-4000 container. The results are shown in

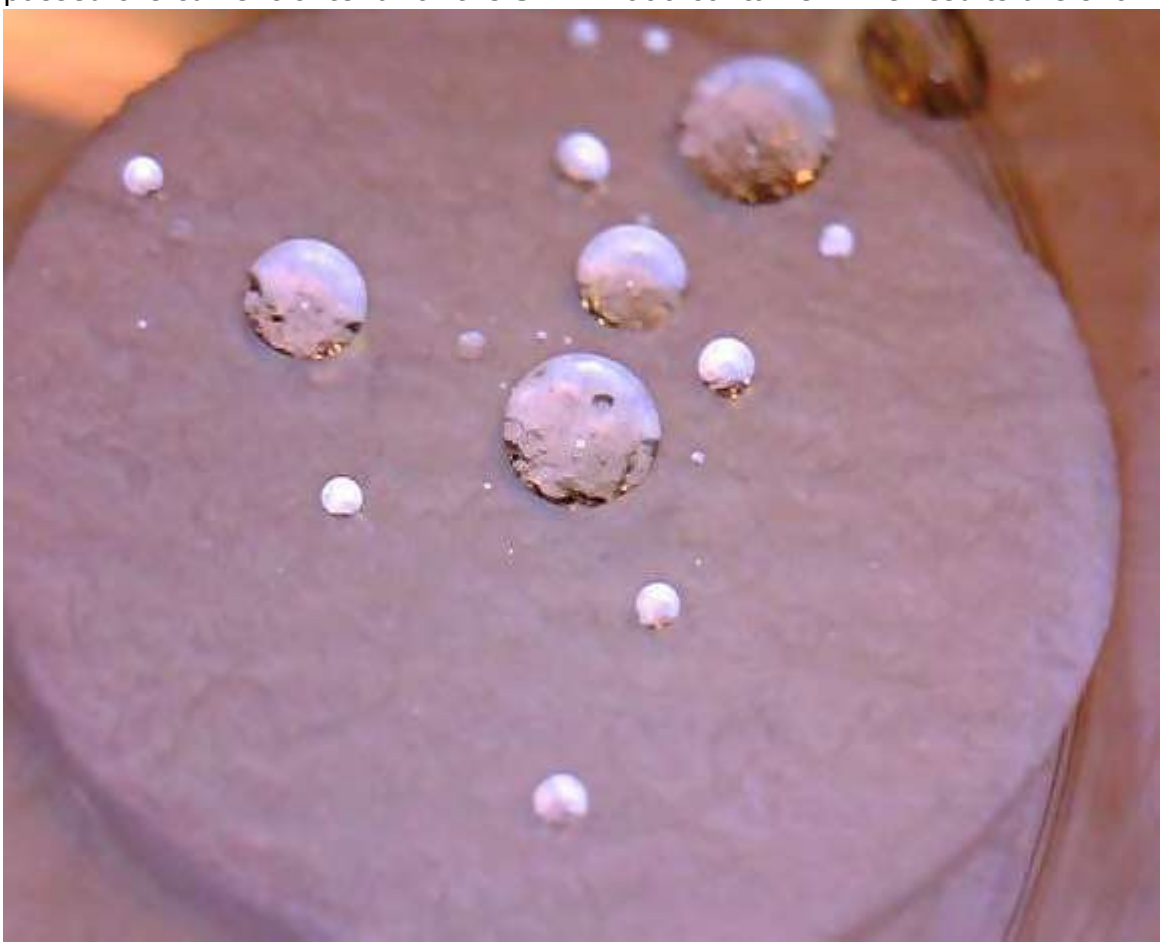

Figure 2. Water droplets beaded on the treated Fiberfrax material.

Table 1. The treated filters all passed a water penetration test at both 6 and 12 inches for a minimum of 60 seconds. [5]

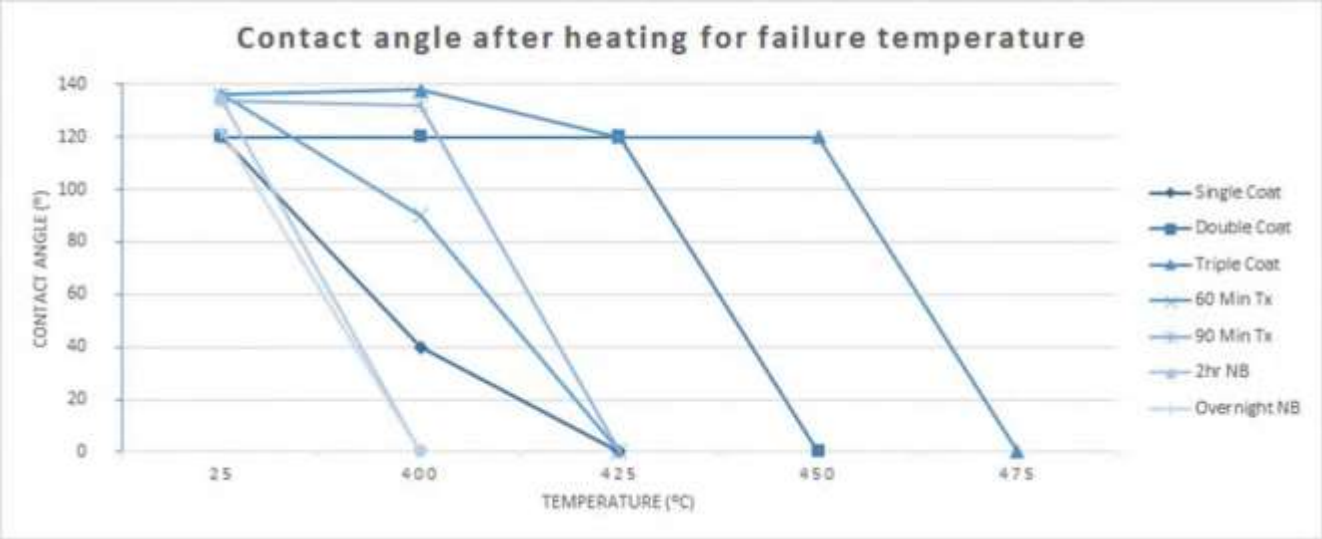

Figure 1. Graph of the various coatings and times and temperatures versus the recorded contact angle.

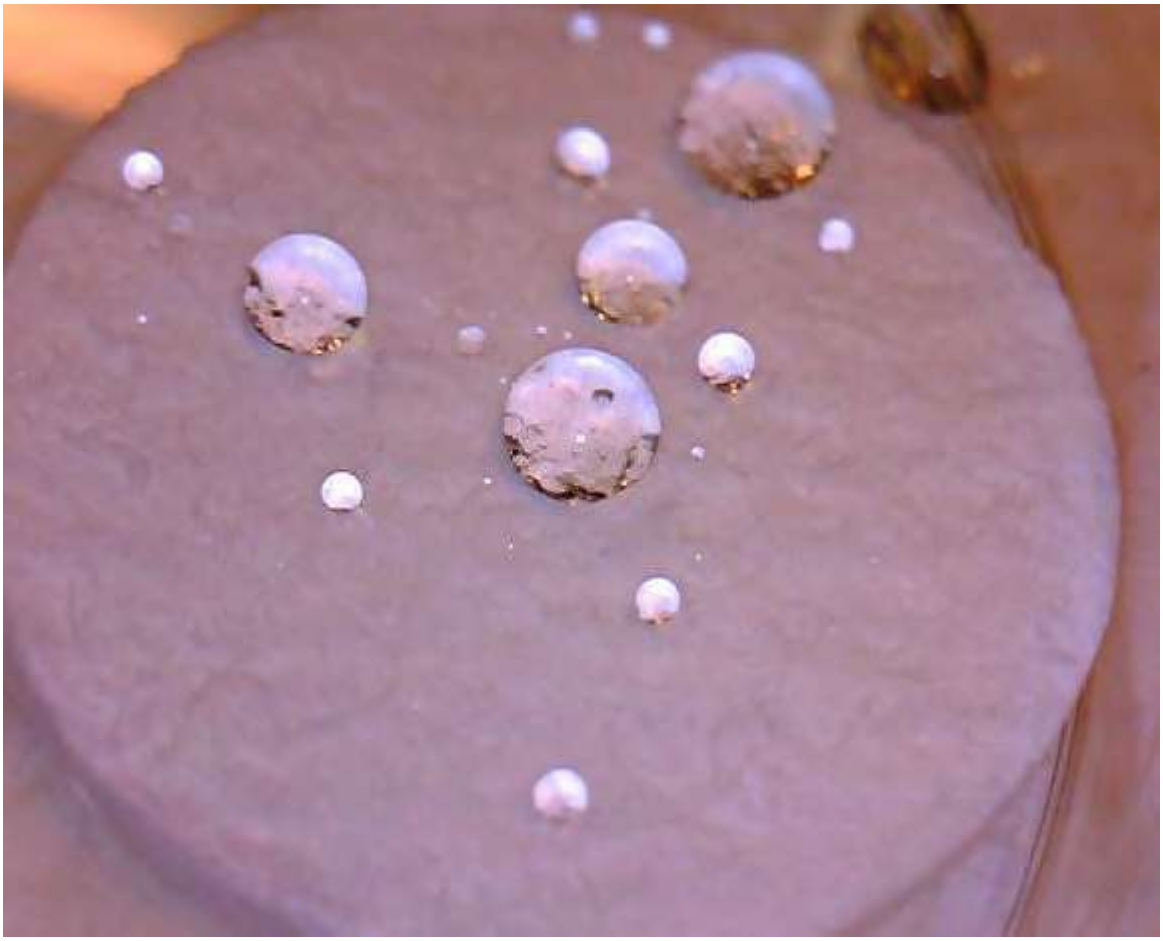

Figure 2. Water droplets beaded on the treated Fiberfrax material.

Table 1. Filtration results for 4 of the various treated Fiberfrax filters.

Sample Number	Percent Penetration	Pressure Drop (in WC)
1	0.0008	0.2
2	0.0005	0.336
3	0.0004	0.338
4	0.0003	0.345

Hydrogen diffusion measurements are not currently available, but, based on the results of the filter testing, it is likely that the material is sufficiently porous to allow hydrogen gas to diffuse through the filter at a rate that meets the requirement.

Discussion

The treated material appears to be passing all of the tests that are required by the current SAVY-4000 test standards. The tests were performed with 1 layer of the treated Fiberfrax but the pressure drop across the filter is similar to a single layer of the filter material used in the SAVY-4000. The treated filter passed the water penetration test at both 6 and 12 inches.

The durability of the treated material still needs to be tested. The Fiberfrax used in current SAVY containers uses a latex binder to hold the filter together. Without this binder, the material becomes more friable. This likely will not be an issue when the filter material is installed in the SAVY-4000 container. When installed, the filter will be sufficiently protected on each side by the lid.

From a broader perspective, nuclear facility and transportation accident scenarios often include fire, impact and subsequent water spray or flooding conditions. Filters for nuclear material containers currently available (and in use at TA-55) depend on carbon composites and/or organic polymers for their water resistant/hydrophobic properties to minimize water ingress and thus mitigate the potential for a criticality event and or subsequent release of contaminated fire suppression water. A purely inorganic hydrophobic filter material would have enhanced resistance to fire and radiation damage, and continue to prevent water ingress, and thus subsequent contaminated water egress, after such an accident. By eliminating the organic elements of the current filters it would make a safer package in the case of fire and high radiation environment

Conclusion

The treated Fiberfrax material maintains the current performance criteria for particulate filteration efficiency, pressure differential, air flow and water penetration. The goal of creating a hydrophobic, inorganic porous material has been met with the treated Fiberfrax material. The treated material maintains hydrophobicity to higher temperatures than the current system used in the SAVY-4000. It is expected that the treated material will have an improved resistance to radioactive degradation.

References

1. Karns, T., et al., *Investigation of Hydrophobic Filter Material for Nuclear Material Transportation and Storage Containers - 16640*, in *Waste Management Symposia ; 2016-03-07 - 2016-03-07 ; Phoenix, Arizona, United States*. 2016, Los Alamos National Laboratory. p. 1 p.
2. Smith, P.H., et al., *Safety analysis report for the SAVY 4000 container series*, in *DOE/NNSA Review*. 2013, Los Alamos National Laboratory.
3. Reeves, K.P., *Development and use of a Low-Flow test system for the filters used in special nuclear material storage containers*, in *INMM Annual Meeting ; 2016-07-24 - 2016-07-24 ; Atlanta, Georgia, United States*. 2016, Los Alamos National Laboratory. p. 1 p.
4. Karns, T., et al., *Gas Permeable Hydrophobic Material*. 2016: United States. p. 37.
5. Karns, T., et al., *Water Ingress Testing for TA-55 Containers*. 2016, Los Alamos National Laboratory. p. 15 p.