Small Scale Drying: FY21 Interim Report

Spent Fuel and Waste Disposition

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SUMMARY

This report documents the FY2021 interim experimental status of small-scale drying tests currently being performed at Pacific Northwest National Laboratory. These small-scale drying tests are intended to develop the technical bases for sensors, techniques, and approaches for determining moisture content from gas samples taken from spent nuclear fuel casks. The need for a better understanding of SNF cask moisture stems from the challenges faced during sampling at the North Anna Nuclear Generating Station for the High Burnup Demonstration Project and guide sampling protocols for dry fuel storage casks. Specifically, the purpose of these tests is to support Sandia National Laboratories gas sample methods and analyses through a series of small-scale experiments. Key focus areas include performing tests to:

- Correlate sample bottle measurements to in-cask conditions
- Estimate the amount of trapped and absorbed water on cask features and surfaces that can contribute to water vapor
- Assess the accuracy of the hygrometer used in the measurements under similar conditions
- Identify and determine the feasibility of additional methods for measuring humidity in casks easily and accurately using lessons-learned from Sandia National Laboratories, including direct gravimetric and isotopic tracer techniques.

To address these topics, a series of five tests were proposed in FY2019. The activities include 1) humidity measurement method development, 2) gas bottle sampling tests, 3) surface drying tests on cladding, 4) small-scale drying of cladding, and 5) small-scale drying of guide-tube/dashpots. A status update was made in the FY2020 interim report (Colburn, 2020). The FY2020 results showed that the sample bottles which were collected did not match the humidity conditions of the pressure vessel. This interim report documents the current progress of these five tests and presents and interprets the results collected in FY2021. To date in FY2021, the bulk of the work was to determine a better configuration and protocol for gas sampling.

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ACKNOWLEDGEMENTS

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ACRONYMS

BWR	boiling water reactor
DIW	deionized water
DOE	US Department of Energy
EPRI	Electric Power Research Institute
FY	fiscal year
HBDP	High Burnup Demonstration Project
PNNL	Pacific Northwest National Laboratory
ppmv	parts per million by volume, a unit of water content
PWR	pressurized water reactor
RH	relative humidity
SNL	Sandia National Laboratories

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SMALL-SCALE DRYING – FY 2021 INTERIM REPORT

1. INTRODUCTION

This project supports the Spent Fuel and Waste Disposition (SFWD) Storage and Transportation thrust area funded under DOE-NE 81 by providing data and measurement methods that are critical to the understanding of the amount of water remaining in a dry storage cask after undergoing the drying process. The driver for this work is based on the wide variability in the sample bottle results obtained from the High Burnup Demonstration Project (HBDP) cask at the North Anna Nuclear Generating Station which was loaded in November 2017. This report provides an interim update for small scale drying activities in FY 2021. All pressures in this report are absolute unless otherwise stated.

The HBDP cask loading and observations are summarized in previous reports and references therein (Colburn, 2020), (Poloski & Colburn, 2019). Briefly, the cask was loaded, excess water siphoned from it, and dried under vacuum for approximately 7 hours. Sufficient dryness was demonstrated by sealing the canister and measuring the interior pressure rise over time (i.e., a “rebound test”). The vacuum used for the rebound test was started at ~0.55 mbar (0.41 Torr). Any pressure increase could be due to leakage, thermal expansion, or gas generation within the cask. The acceptance criterion is that the pressure remains below 4 mbar (3 Torr) after 30 minutes (Jung, et al., 2013). The observed linear pressure increase from the demonstration cask could indicate a gas-generation mechanism, such as evaporation or desorption, that is limited by mass or heat transfer. Additionally, more complex phenomena can occur via radiolytic gas generation (Spinks, 1990).

The primary goal of the demonstration project was to evaluate the effects of dry storage on high burnup fuel, but a secondary goal was to evaluate the gas composition within the cask and how it changes over time. After drying, the canister was backfilled with He to 2.2 bar. Two sets of gas samples were collected each at ~5 hours, ~5 days, and ~12 days after closure. The samples were collected in 1-L stainless steel sample bottles that were pre-conditioned to remove water from the bottle interior. The main goal of the gas sampling was to verify the efficiency of the drying process used for the dry storage cask. As discussed in previous reports (Colburn, 2020) (Poloski & Colburn, 2019), there were discrepancies in the water content measurements from the sample bottles which led to this current effort.

Bryan et al. (Bryan, et al., 2019) report that a 17 × 17 pressurized water reactor (PWR) cladding assembly has about 30.6 m^2 and 43.5 m^2 of cladding and total zircalloy assembly surface area. For a full cask with a 32 assembly array, this equates to roughly 980 m^2 and 1400 m^2 of cladding and total assembly surface area, respectively. Assuming that a water loading of approximately 10 $\mu g/cm^2$ (0.1 g/m^2) is representative of the surface, this would equate to 98 g of water sorbed on the cladding and another 42 g of water sorbed on other assembly components, for a total of 140 g. It is unclear how much of this water is liberated through the vacuum drying process and could remain in the backfilled cask during storage. Note that these water vapor estimates are only from physisorbed water on the zircalloy assembly components. Bryan et al. (Bryan, et al., 2019) describe several potential sources of water vapor including:

- Bulk water trapped in assembly components that is released after final backfill
- Water trapped in dashpots, where limited gas exchange could make removal difficult
- Water in failed fuel rods
- Boric acid hydrates that precipitated from undrained pool water during the drying process
- Water trapped in Boral®, a porous neutron absorber material used in many dry storage systems
- Structural and adsorbed water associated with crud, a colloquial term for corrosion and wear products that may coat the water-side of cladding

- Structural water associated with hydrated corrosion products in the canister
- Chemisorbed and physisorbed water.

Liberation of chemisorbed and physisorbed water is expected to require elevated temperatures, a reduction of relative humidity or a combination of the two. Hanson (Hanson, October 24, 2018) provides measured fuel assembly temperatures through the HBDP cask drying process as 100–237°C during vacuum drying and 120–229°C after backfilling with helium. The cladding temperatures are expected to rapidly increase during the vacuum drying phase and reach a maximum just prior to backfilling. While at the elevated temperatures, water desorption could occur for many hours. It is important to note that there are significant temperature gradients within the cask, and these values represent a nominal maximum value with much lower values near the cask outer wall. Bryan et al. (Bryan, et al., 2019) consider Boral® components to be of particular interest as a source of water vapor due to its porous structure with high surface area. Boric acid precipitates at the bottom of a cask could also be a source of water vapor that might be difficult to remove especially if the deposits are in a lower temperature region during vacuum drying.

2. PROJECT PURPOSE AND OBJECTIVES

The purpose of the testing activities and test results presented in the current report is to support Sandia National Laboratories (SNL) gas sample methods and analyses through small-scale experiments. Key focus areas include testing to:

- Correlate sample bottle measurements to in-cask conditions
- Estimate the amount of trapped and absorbed water on cask features and surfaces identified by Bryan et al. (Bryan, et al., 2019) that can contribute to the presence of water vapor
- Assess the accuracy of the Vaisala hygrometer under a wider array of temperatures, water vapor concentrations, and gas environments than those evaluated during the initial Bryan et al. validation tests (Bryan, Jarek, Flores, & Leonard, 2019). Explore other potential hygrometer technologies for use in this application.
- Determine the feasibility of additional methods for measuring humidity in cask easily and accurately using lessons-learned from the Bryan et al. (Bryan, Jarek, Flores, & Leonard, 2019) report including direct gravimetric and isotopic tracer techniques.

There are two main objectives to the testing activities on this project. The first objective is method development in sampling and quantifying the amount of water in the cask system. Some key questions for this objective include:

- How accurate/precise is the humidity instrumentation?
- How does condensation in sample bottles affect measurement?
- Does helium gas affect measurements?

A second objective is to identify the source of water in the gas samples. Some key questions for this objective include:

- How much water can be added to the cask headspace from sorption layers on the cladding material? It is believed that crud would contribute water to the system in a similar way to the oxide layers on cladding.
- Can the water be coming from a liquid source from the guide-tube/dashpots (i.e., the dashpot drain holes potentially becoming obstructed with boric acid or other precipitates known as crud)?

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3. TEST APPROACH AND INTERIM RESULTS

Five tests, designated Tests A–E, were developed in FY2019, were started in FY2020, and are in progress to support the test purpose and objectives. They are described in more detail in the following subsections with slight changes from previous reports as the work has evolved. The five tests are described below:

- *Test A, Method Development and Sample Bottle Loading* – The purpose is to increase confidence in the sampling and measurement sensor technology used for the demo cask humidity results.
- *Test B, Sample Bottle Measurements* – The purpose is to increase confidence in the sampling measurement approach used by SNL for the demo cask humidity results through a PNNL/SNL inter-laboratory comparison of results from gas samples taken from controlled conditions using saturated salt solutions to achieve target humidity levels. It was also planned for this test to employ lessons-learned documented by Bryan et al. (Bryan, Jarek, Flores, & Leonard, 2019) for using an isotopic tracer and gravimetric measurements as alternative approaches for water vapor measurements from the gas samples. However, preliminary calculations indicate that this approach of liquid water trapping followed by isotopic analysis may not be feasible. Further detail is provided in section 3.2 below.
- *Test C, Surface Drying Tests* – The purpose is to gravimetrically measure the amount of water desorbed from the surface of oxidized cladding material, over a temperature range consistent with measurements made in the HBDP cask during vacuum drying.
- *Test D, Small-Scale Drying of Cladding* – The purpose is to assess backfill gas humidity derived from desorption of water from the surface of cladding material before and after vacuum drying at a temperature consistent with measurements made on the HBDP cask during vacuum drying.
- *Test E, Small-Scale Drying of Guide-Tube/Dashpots* – The purpose is to assess backfill gas humidity derived from water accumulated in a mockup of a guide-tube/dashpot before and after vacuum drying at a temperature consistent with measurements made on the HBDP cask during vacuum drying.

3.1 Test A – Method Development and Sample Bottle Loading

Testing done in support of method development and sample bottle loading have been previously reported in detail (Colburn, 2020). Briefly, the Vaisala HMP4 variable capacitance relative humidity probe was installed into a sealed container and tested at different conditions using a 36-point test matrix evaluating the impact of temperature, pressure and salt solution on measured humidity. . The hygrometer was found to be most accurate when mounted directly in the headspace of the pressure vessel; however, the manufacturer recommends the probe be mounted horizontally which was not feasible in the configuration as tested in FY2020. In FY 2021, a new pressure vessel was ordered from Alloy Products to accommodate the humidity probe in a horizontal configuration. In addition, a second humidity probe was acquired so the probe configuration (horizontal vs. vertical) could be simultaneously compared directly in the same vessel headspace. Due to the COVID-19 pandemic, the purchasing and fabrication of the vessel was delayed. The vessel was received by PNNL in March 2021. The photo shown in Figure 1 shows the new 1-gallon vessel with both humidity probes installed, one vertical, one horizontal.

Figure 1. Custom fabricated 1 gallon pressure vessel with two Vaisala HMP4 probes installed.

To replicate planned cask gas sampling activities, the testing of the 1-gallon vessel shown in in Figure 1 included a series of gas sampling events. Here, headspace gas was drawn into sample collection bottles pretreated to remove initial residual water. In FY 2020 the sample bottles did not match the humidity conditions in the test vessel. In FY2021, a variety of sample loading configurations were tested to determine the optimal configuration and protocol for testing.

3.1.1 Key Test Details and Results

Performing the bottle loading configuration tests required the use of different ovens and environmental chambers that were capable of holding most of, or preferentially all, of the apparatus to determine the optimal configuration for loading bottles. As such, the following ovens and chambers were used in the course of the work to date in FY2021:

1. VWR model 1350 FM oven (internal dimensions 18.25” wide, 19” deep, 16.5” high)
2. Fisher IsoTemp 179L Forced air convection oven (internal dimensions 18.3” wide, 21.4” deep, 27.9” high)

3. Large environmental chamber in the 318 building at PNNL(internal dimensions 5’ wide, 5’ deep and 7’ high)
4. Medium environmental chamber in the 318 building at PNNL (internal dimensions are nearly identical to the Fisher IsoTemp oven).

The pressure vessel was manufactured by Alloy Products Corporation out of 316L stainless steel with a 1-gallon capacity and is American Society of Mechanical Engineers stamped with a rating full vacuum to 132 psig at 150°C. A 4-gallon pressure vessel, also manufactured by Alloy Products Corporation was also used for one of the configuration tests discussed below. The thermocouples selected are 304 Stainless Steel Omega type-K (item #TJ36-CASS-116U-24) capable of measuring the temperature of the gas phase ±2°C. A data acquisition system was used to measure and record the data at 1 measurement/min. The data acquisition system selected is the Red Lion Controls master controller (model #CSMSTRGY) with modules for proportional–integral–derivative control (model # CSPID2R0), thermocouple input (model #CSTC8000), and current signals (model #CSINI800). Pressure transducers that are capable of measurements from 0 to 8 bar were needed. The pressure transducers selected are Omega high-accuracy oil-filled transducers, model numbers PX409-005AI, PX409-050AI, and PX409-150AI. They cover three pressure ranges, 0–5 psia, 0–50 psia, and 0–150 psia with an accuracy of 0.8% of full scale. The humidity sensors are Vaisala probe model HMP4. Swagelok 300 cm^3 U.S. Department of Transportation compliant 316 stainless steel sample bottles were selected for this test, both bare stainless steel and Teflon®-lined bottles were used in testing. A Welch 1400 vacuum pump capable of achieving pressures to 10^{-3} bar also was used. In addition, high purity helium gas, 18 MΩ resistivity deionized water (DIW), and reagent grade or better NaCl were used. The data acquisition system (including thermocouples, pressure transducers and humidity sensors) was calibrated by PNNL’s NVLAP accredited laboratory before testing was started using NIST traceable standards for temperature, pressure and humidity.

One of the first steps for Test A was to pre-treat sample bottles by heating them in the VWR oven. The oven was set to 100°C and the samples were heated for 16–24 hours. During this time, the sample bottles were evacuated to less than 10 Torr. The quarter-turn valves connected to the sample bottles were worked during pumping to remove as much air as possible. Then the valves were closed to isolate the bottles for storage and the bottles were stored in at room temperature until use.

Approximately 1L of water was placed in the pressure vessel. The pressure vessel was sealed and placed in the oven. Tubing connections were made, and the thermocouples in the pressure vessel were placed in the correct positions. The data acquisition system was started to record pressure, temperature, and hygrometer data. A vacuum was momentarily pulled—nominal pump rating of approximately 30 Torr — to remove residual air. The pressure vessel was backfilled with helium cover gas to approximately 2.2 bar, and the oven was set to 30°C. The cover gas was bled off as necessary to maintain the desired pressure during heating. The system was allowed to equilibrate overnight. When the pressure, temperature, and hygrometer readings as % relative humidity (%RH) had stabilized, data were manually recorded. Samples of the pressure vessel headspace were collected in the pretreated sample bottles. The valves to the sample bottles were opened to draw the sample, waiting several minutes for pressure re-stabilization, and then the valves were closed. Again, pressure, thermocouple, and hygrometer data were recorded manually. Several configurations were tested as shown in the Figures 2-4.

In FY2020, the measurements from the pressure vessel headspace samples were roughly 10-20% of the measured humidity in the pressure vessel in 5 out of the 6 measurements taken. Based on the configuration used for sampling in FY2020 (Colburn, 2020), it was assumed that humidity was being lost through condensation when the valves were opened to the evacuated bottle causing cooling due to the rapid expansion. Therefore, the initial goal was to minimize the amount of tubing between the vessel and the sample bottle. The configuration shown in Figure 2 was assembled in the medium-sized environmental chamber in the 318 building at PNNL. This chamber was large enough to accommodate a sample bottle connected directly to the pressure vessel. In an attempt to make the apparatus fit into the existing oven, this was replicated with a 15” length of tubing between the vessel and the sample bottle as shown in Figure 3. The water in the gas sample bottles was measured as described below in section 3.2 below. None of the bottles from these configuration tests showed a marked improvement over the observations in FY2020.

Figure 2. Initial FY2021 bottle sampling configuration test. The sample bottle was connected directly to the pressure vessel to minimize water losses to tubing during expansion.

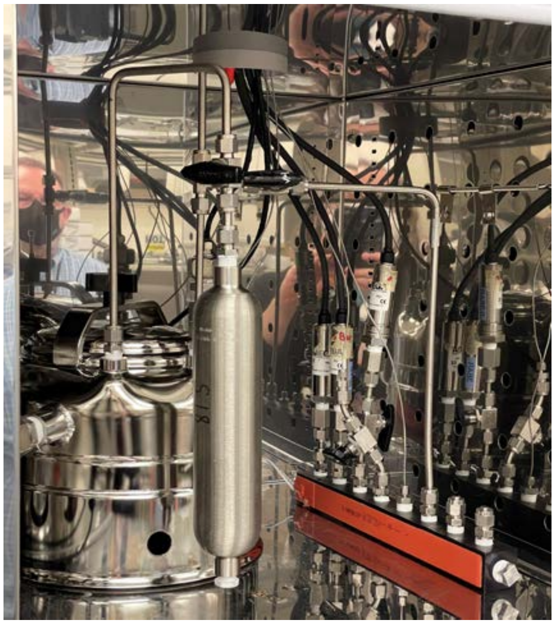

Figure 3. FY2021 Configuration testing, VWR oven, 15” length of tubing between the sample bottle and pressure vessel.

Upon closer observation of the photos from the demo cask sampling, the bottles that were used in the demo cask had valves at both ends and were connected in a serial fashion for sampling. The photo in Figure 4 shows the first test with bottles valved at both ends connected together. This test was repeated with a heated blanket covering the portion above the oven with a thermocouple in place to determine the temperature of that heated zone. The water in the gas sample bottles was measured as described in section 3.2 below. Again, these bottles did not show a marked difference from the results observed in FY2020 (Data not shown but unreviewed data is available for discussion). Note that for this test both humidity probes were located in the pressure vessel, so the humidity level at the point of sampling was not known.

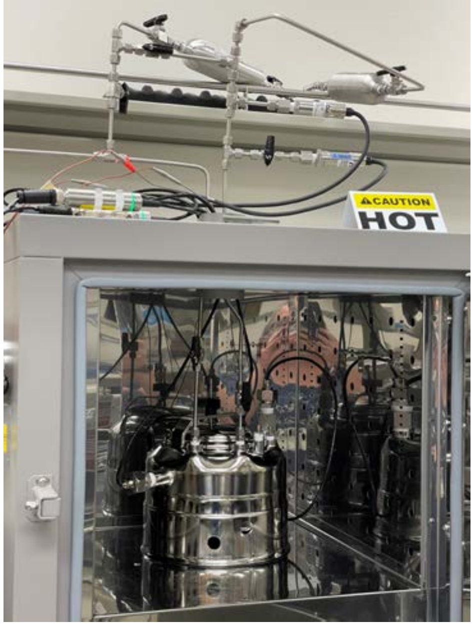

Figure 4. FY2021 Sample bottle configuration testing – VWR oven, two sample bottles in a double-ended configuration this test was repeated with a heated blanket around the upper portion.

In order to gain a better understanding of the behavior of the humidity in the system, the system was reconfigured again to place a second humidity probe above the sample bottle which was mounted directly to the pressure vessel in a vertical configuration as shown in Figure 5 and Figure 7. The second humidity probe was mounted such that the probe end was as close to the end of the sample bottle as possible. Testing with this configuration involved evacuating the top humidity probe portion in addition to the pressure vessel. The top probe portion remained under vacuum while the pressure vessel was backfilled with helium to approximately 2.2 bar pressure. Once the vessel was at equilibrium, the sample bottle valves were opened, and the humidity was observed. The desired goal was for the humidity of the top probe portion would match that of the humidity of the probe reading from the headspace of the pressure vessel.

Figure 5. Large environmental chamber with 4-gallon pressure vessel. Second humidity probe mounted horizontally above the outlet of the sample bottle.

The test in the large chamber ran for approximately 4 hours after an overnight equilibration in the chamber to come to temperature. The results from the large chamber bottle fill test are shown in Figure 6, where the blue dots show the absolute humidity readings from the humidity probe inside of the pressure vessel, while the red dots show the humidity probe readings from the probe located above the sample bottle. The nominal absolute humidity in saturated helium at the experimental conditions at 0.5 hrs of 28.8°C and 2.37 bar pressure is 28.4 g/m^3 as calculated using the Michell Humidity Calculator (http://www.michell.com/calculator/). The experimental value of 28.6 g/m^3 for the vessel headspace at this time point is within the stated uncertainty of the Vaisala humidity probe. Note that in the plots shown in this section, there appears to be periodic spikes in the humidity probe readings that are not well understood at the time of this report. The results from subsequent testing of the bottle are discussed in section 3.2. Due to scheduling constraints, the apparatus had to be removed from the large chamber, so the apparatus was replicated with the 1-gallon pressure vessel in the medium environmental chamber as shown in Figure 7.

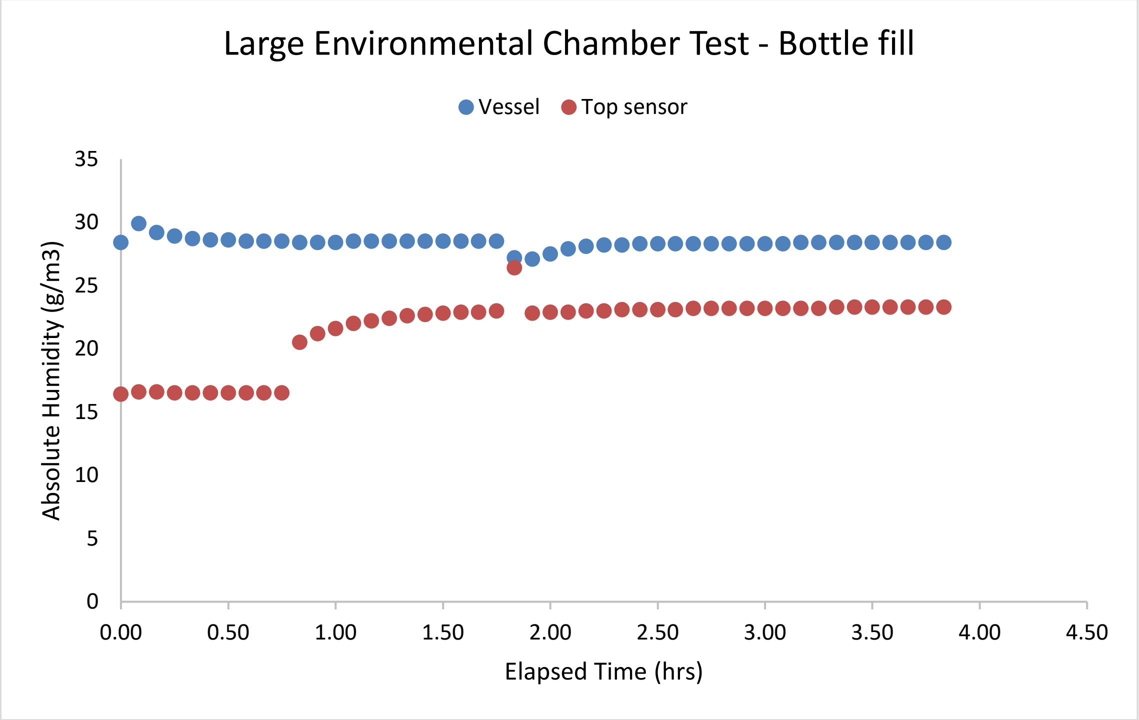

Figure 6. Vaisala humidity probe results from the large environmental chamber experiment as shown in Figure 5.

Figure 7. Similar to the system shown in Figure 5, but with the 1-gallon pressure vessel in the medium environmental chamber.

The bottle fill test in the medium environmental chamber was executed with water in the pressure vessel. The humidity probe readings are plotted in Figure 8 where the blue line is the humidity in the headspace of the vessel while the red line is the humidity readings from the assembly above the sample bottle. The two sensors did not reach agreement after more than 4 days of testing, they were offset by approximately 4 g/m^3. The temperature sensor internal to the humidity probe in the pressure vessel had an average reading 0.3 to 0.4°C higher than the temperature sensor internal to the humidity probe in the upper portion of the apparatus. Specifically, at 89 hours into the experiment, the system pressure was 2.36 bar, the temperature of the probe in the vessel was 30.6°C while the vessel headspace type K thermocouple read 29.1 ± 2°C. The temperature of the probe in the upper apparatus was 30.3°C, no additional temperature measurement was made in this portion of the system. This temperature offset in a saturated helium system would lead to absolute humidity conditions of 31.36 g/m^3 in the vessel at 30.6°C and 30.85 g/m^3 in the apparatus at 30.3°C respectively [a difference of ~0.5 g/m^3] based on calculations made using the Michell Humidity Calculator (http://www.michell.com/calculator/). The Vaisala HMP4 probes have a vendor-stated temperature uncertainty of ± 0.1°C. With the uncertainty of the probe in the vessel, the absolute humidity could range from 31.19 to 31.52 g/m^3, and the absolute humidity in the upper portion of the system could range from 30.69 to 31.02 g/m^3. The vendor-stated uncertainty for the humidity probes is ±0.8%RH which equates to approximately ±0.5 g/m^3 in the saturated system at 30°C and 2.36 bar. Therefore, the temperature offset between the two probes does not entirely explain the difference between the two readings.

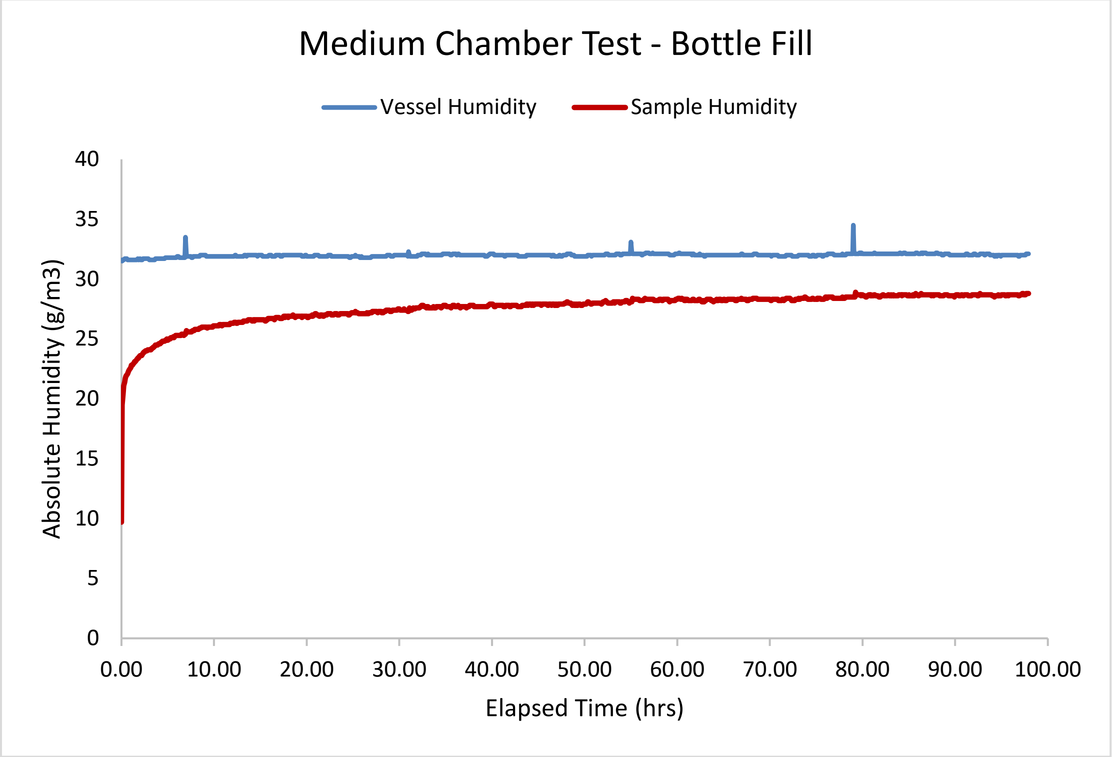

Figure 8. Vaisala humidity probe results from the medium environmental chamber experiment as shown in Figure 6. At the end of the experiment, the probe readings are offset by approximately 4g/m^3 absolute humidity.

The 1-gallon version of the configuration was assembled in the Fisher IsoTemp 179L oven as it was large enough to accommodate the apparatus. At this time, small changes were made to the system such as moving one of the pressure transducers to the top probe portion of the system which are not shown in the photos here (see Figure 7). The next test conducted had tubing in place of the sample bottle to determine if the reduced surface area would improve the agreement between sensors. Figure 9 shows the Vaisala humidity readings from this test where the blue line shows the readings from the probe in the vessel headspace while the red line is the humidity probe readings from the assembly above the tubing. After more than 6 days the two sensors did not reach agreement but were still offset by about 3 g/m^3. This smaller observed offset at the end of the test could be explained by the smaller surface area of the tubing as compared to the sample bottle.

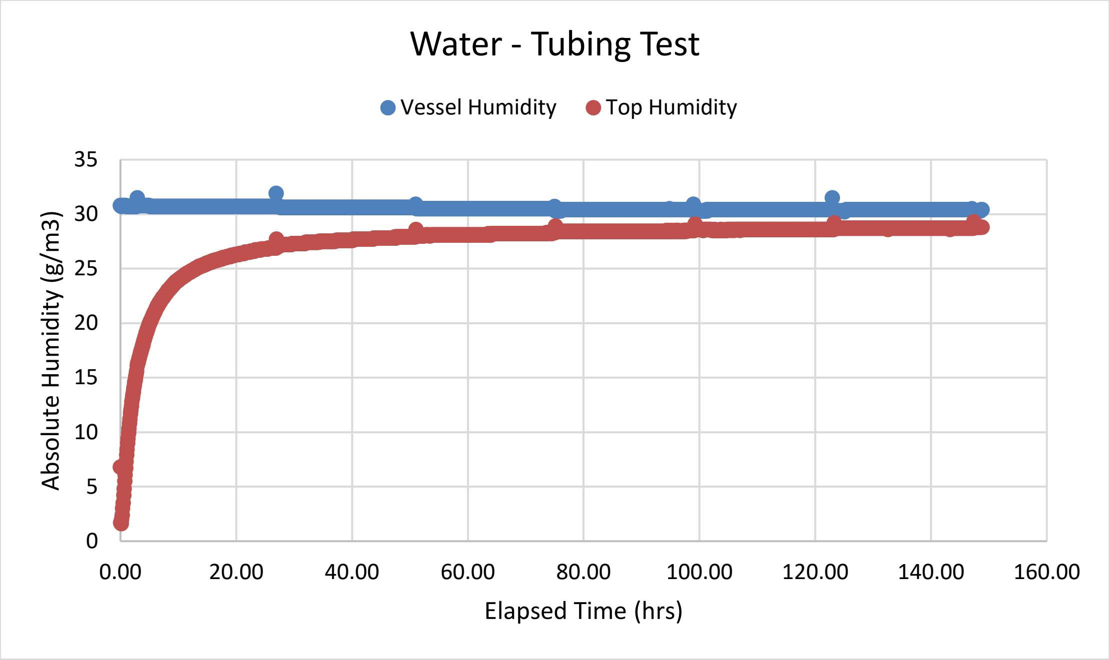

Figure 9. Vaisala humidity probe readings from the system with tubing in place of the sample bottle. At the end of the experiment the probes are offset by approximately 3 g/m^3 absolute humidity.

A saturated sodium chloride solution was tested as well to understand if a reduced humidity level would improve this agreement. Figure 10 shows the Vaisala humidity readings from this test where the blue line shows the readings from the probe in the vessel headspace while the red line is the humidity probe readings from the assembly above the tubing. The nominal absolute humidity of the system at the probe temperature and vessel pressure at the end of the experiment is 24.1 g/m^3. The two probe readings are offset by 0.7 g/m^3 which is likely within the error of the probes. The slope of the blue line is not well understood at the time of this report.

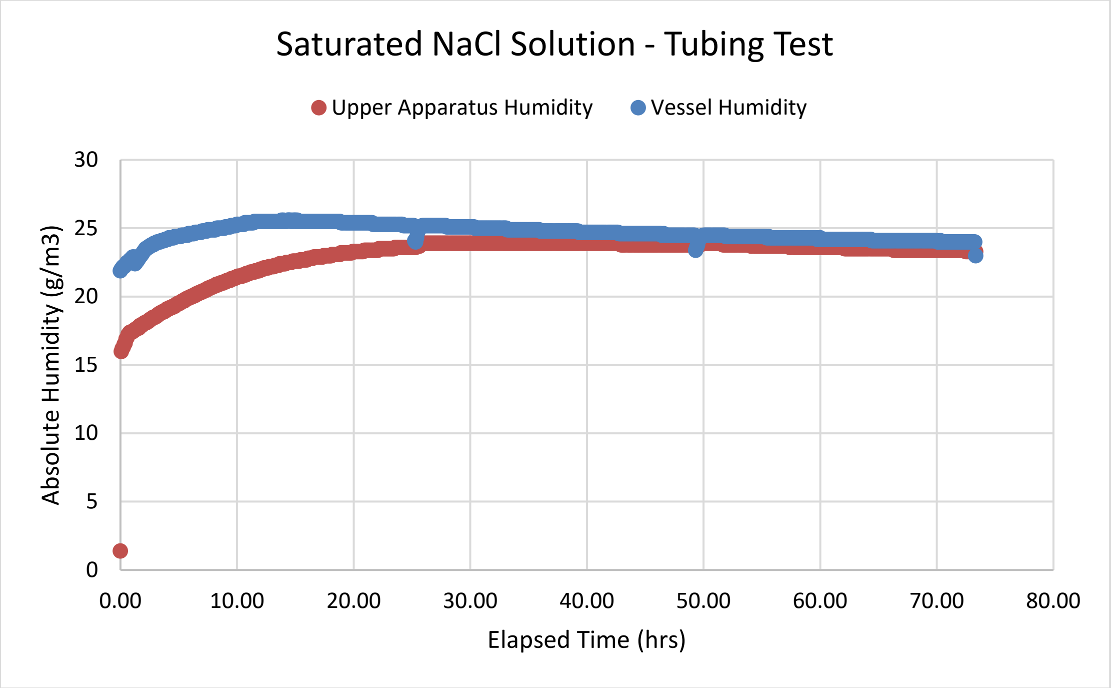

Figure 10. Vaisala humidity probe readings from the system with tubing using saturated sodium chloride to regulate the humidity in system.

A sample bottle was used in the place of the tubing in the system to collect sample bottles from the headspace of the saturated sodium chloride solution in the pressure vessel. Figure 11 is the Vaisala humidity probe readings from this bottle fill where the blue line is the vessel headspace humidity probe readings and the red line is the humidity probe readings from the assembly above the sample bottle. Since the sodium chloride salt system humidity was not saturated as with the water-only systems, the assumption was that this test would reach equilibrium and the two probes would reach the same reading. The offset (0.8 g/m^3) between the two probes at the end of the test is within the error of the humidity probes.

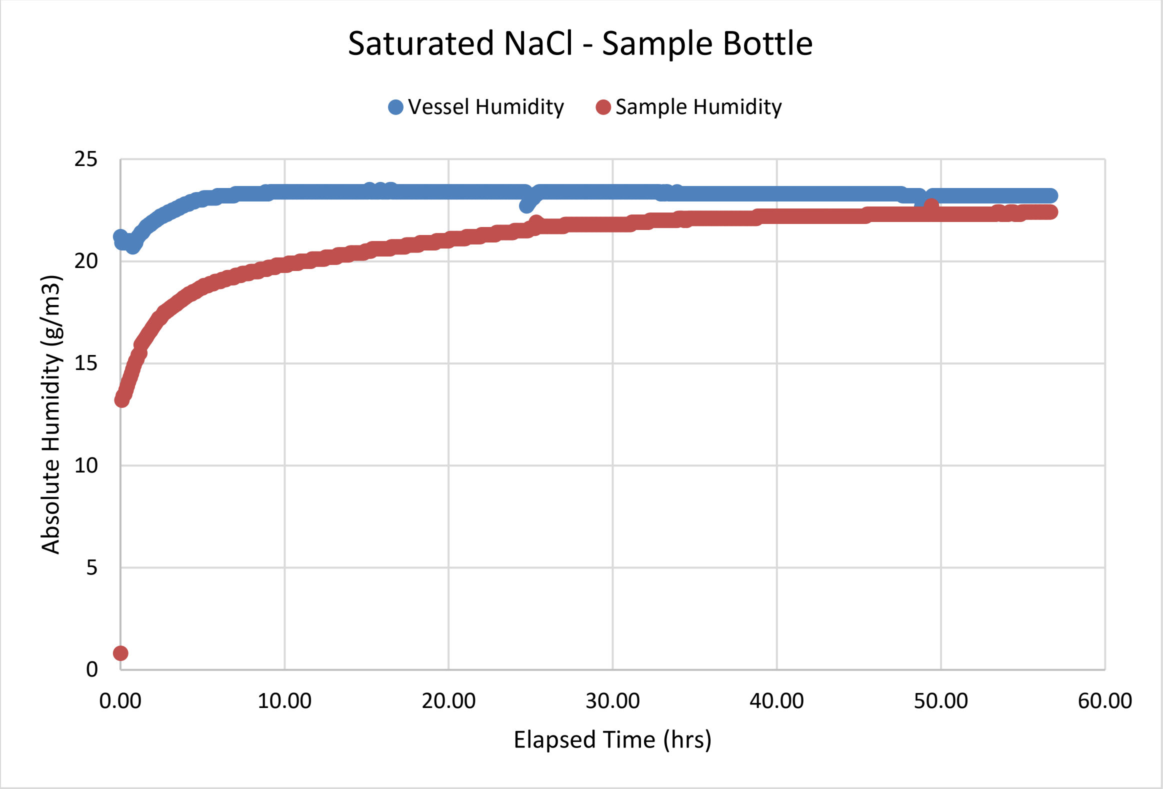

Figure 11. Vaisala humidity probe readings from the saturated sodium chloride system sample bottle fill.

Finally, Teflon-lined sample bottles were tested to see if probe agreement would improve or impact sample bottle measurements as discussed in section 4.2. The Teflon bottle test was repeated because the helium supply ran out towards the end of the test. The bottle fill humidity readings are plotted in Figure 12 and Figure 13. In Figure 12, the offset between the two probes is 1.3 g/m^3 just before the helium supply ran out in the system, again this could be argued to be within the error of the humidity probes. In Figure 13, the second Teflon-lined bottle, the offset is 1.2 g/m^3 at the end of the experiment, again, this is likely within the error for the system. Again, a slight negative slope was observed in the vessel humidity readings over the course of these experiments which is not well understood at this time.

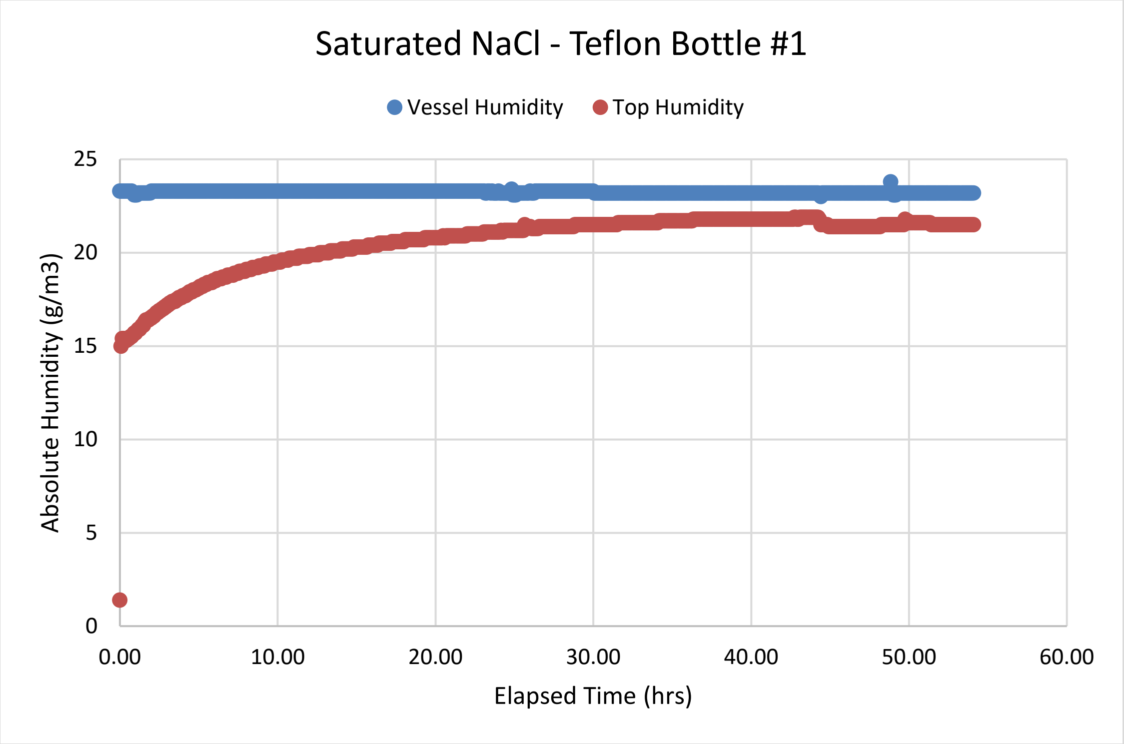

Figure 12. Vaisala humidity probe readings from the saturated sodium chloride system sample Teflon-lined bottle fill #1.

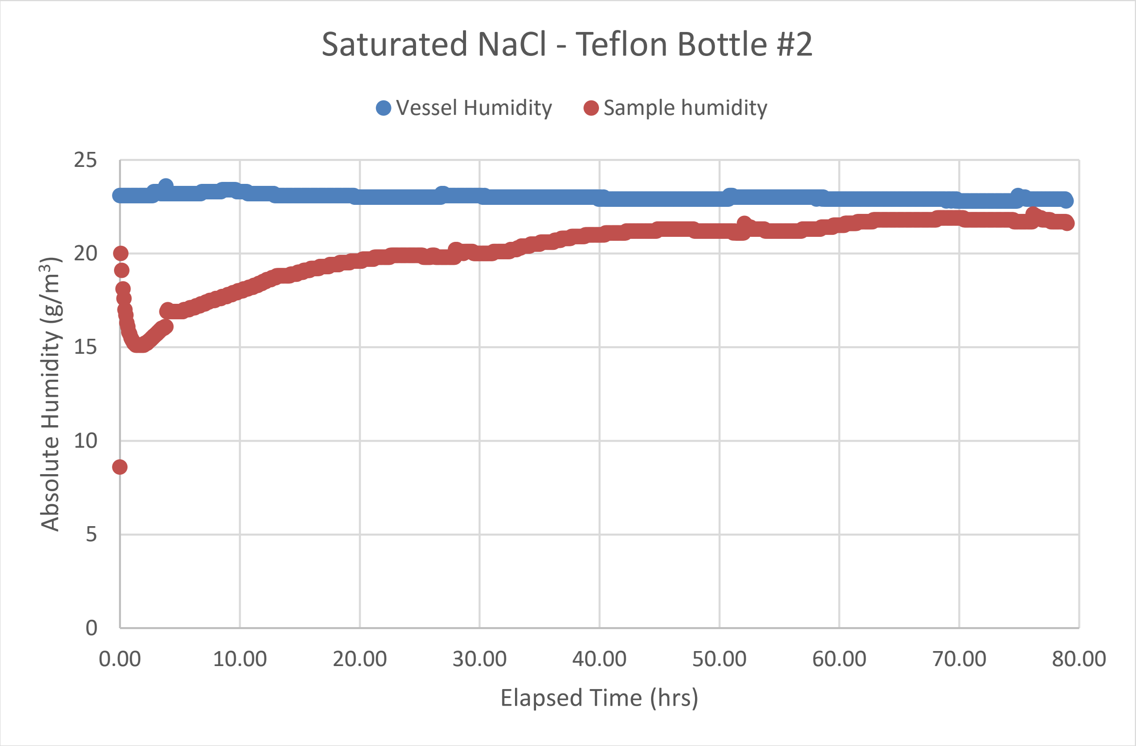

Figure 13. Vaisala humidity probe readings from the saturated sodium chloride system sample Teflon-lined bottle fill #2.

3.2 Test B – Sample Bottle Measurements

This test series is designed to increase confidence in the sampling measurement approach used by SNL for the demo cask humidity results through a PNNL/SNL inter-laboratory comparison of results from gas samples taken from controlled conditions using saturated salt solutions to achieve target humidity levels. Once the bottle fill protocol is finalized, the sample bottles will be filled for inter-laboratory comparison.

Additionally, the test intended to employ lessons-learned documented by Bryan et al. (Bryan, Jarek, Flores, & Leonard, 2019) for using an isotopic tracer and gravimetric measurements as alternative approaches for water vapor measurements from the gas samples, see FY2020 report for details (Colburn, 2020). Preliminary calculations show that the 300 mL sample bottles are likely to contain less than 10 microliters of liquid water when filled from a 30 g/m^3 humidity level environment. This presents some challenges for trapping the liquid water in the bottles.

3.2.1 Key Test Details and Sample Bottle Measurement Results

Sample bottles are measured by removing the pressure vessel from the oven and connecting the sample bottle to a manifold which is equipped with a thermocouple, pressure transducers, and one humidity probe similar to the system shown in Figure 14. The manifold is evacuated overnight in an oven set to 30°C. The sample bottle valve is opened to the manifold and humidity readings are taken while the oven temperature is increased at 10°C intervals every 30-45 minutes to 100°C with a final 30-45 minute hold time. Data was automatically collected at 5-minute intervals by the data acquisition system. Future work is warranted exploring the optimal temperatures for sample bottle measurements, as well as how long a system needs to be evacuated, hold times, and minimizing the surface area of the manifold.

Figure 14. Manifold assembly for measuring humidity in sample bottles.

The first sample bottle tested was from the large chamber test shown in Figure 5, with the bottle fill humidity readings shown in Figure 6. Note that this bottle fill likely did not reach equilibrium. The bottle test results are shown in Figure 15. The slight 'bump' in the curve at ~70°C is due to a longer equilibration time at that temperature point. The absolute humidity readings from the bottle at 100°C (23.5 g/m^3) are slightly greater than the final reading taken in the assembly above the sample bottle (23.3 g/m^3) during the fill. These values were promising given the low readings that were observed in FY2020. Note that during testing of the bottles, they did not reach equilibrium within the 30-45 minute hold time as demonstrated by the long equilibration times as observed when filling (see Figure 6). However, the methodology used would be more realistic for testing bottles sampled from spent fuel casks and correlating those values to in-cask conditions. Further studies on the equilibration times of the bottles at different temperatures are warranted based on the results observed during FY 2021.

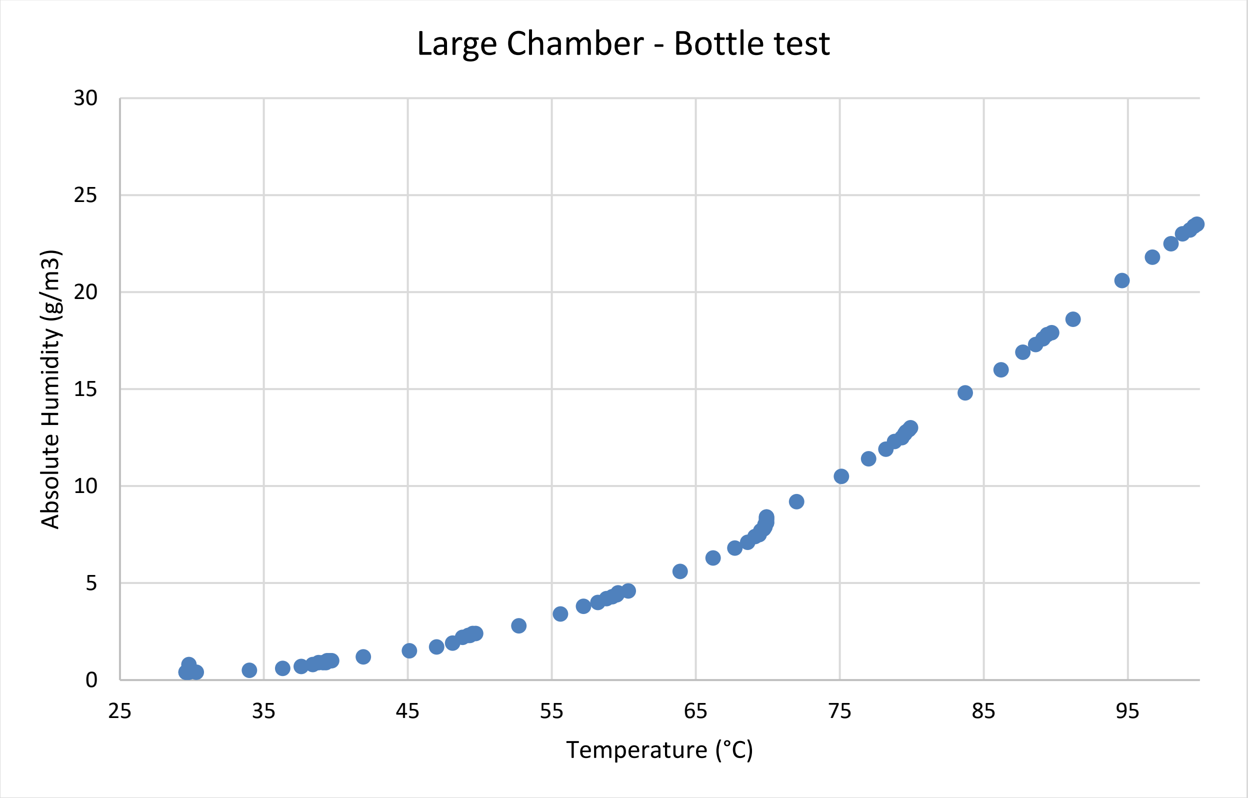

Figure 15. Bottle humidity measurements as a function of temperature from the large environmental chamber test.

The next test was the sample bottle from the medium chamber test shown in Figure 7, with the bottle fill humidity readings shown in Figure 8. The bottle test results are shown in Figure 16. An initial spike in humidity was observed when the sample bottle valve was opened to the evacuated manifold followed by a decrease during the hold time at 30°C. This is likely due to water being adsorbed on the surfaces of the manifold immediately following the expansion of the sample into that portion of the system. The absolute humidity readings from the bottle at 100°C (30.2 g/m^3) are greater than the final reading taken in the assembly above the sample bottle (28.8 g/m^3).

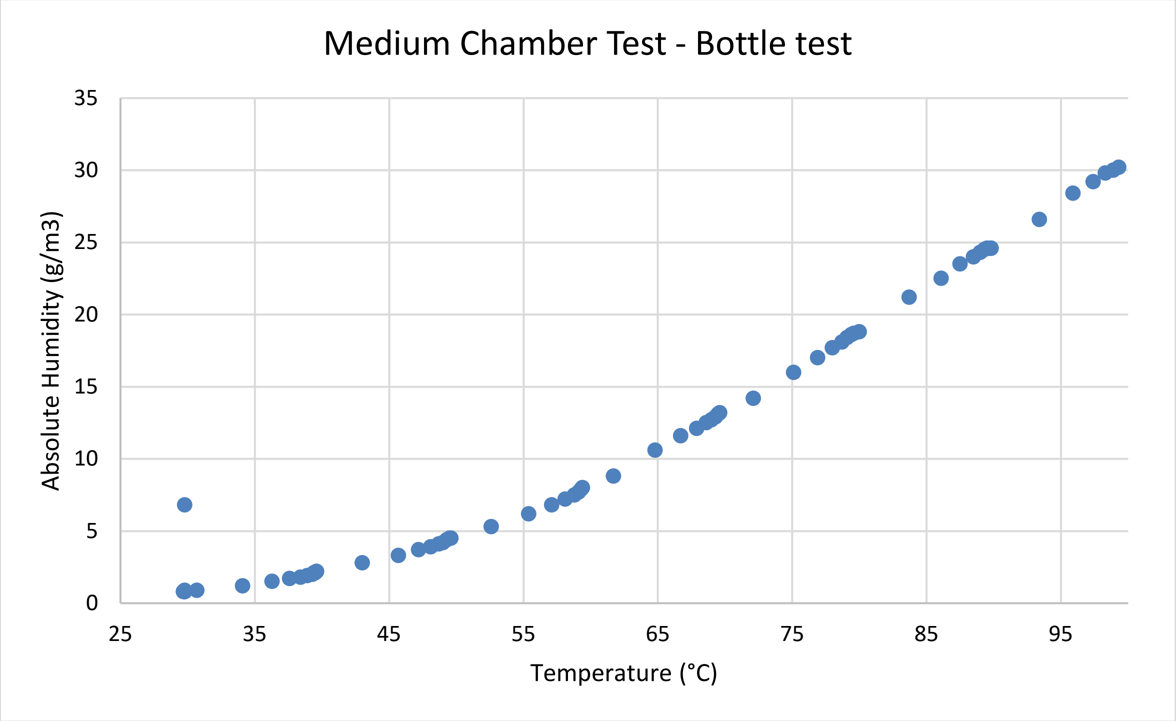

Figure 16. Bottle humidity measurements as a function of temperature from the medium environmental chamber test.

The next sample result shown in Figure 17 is the sample bottle from the saturated sodium chloride test. The bottle fill humidity readings shown in Figure 11. The bottle test results are shown in Figure 17. Unlike the bottle measurement shown in Figure 15, the ‘jump’ in the data at approximately 70°C is not well understood as the hold time was not extended at this temperature. The absolute humidity readings from the bottle at 100°C (24.8 g/m^3) are greater than the final reading taken in the assembly above the sample bottle (22.4 g/m^3).

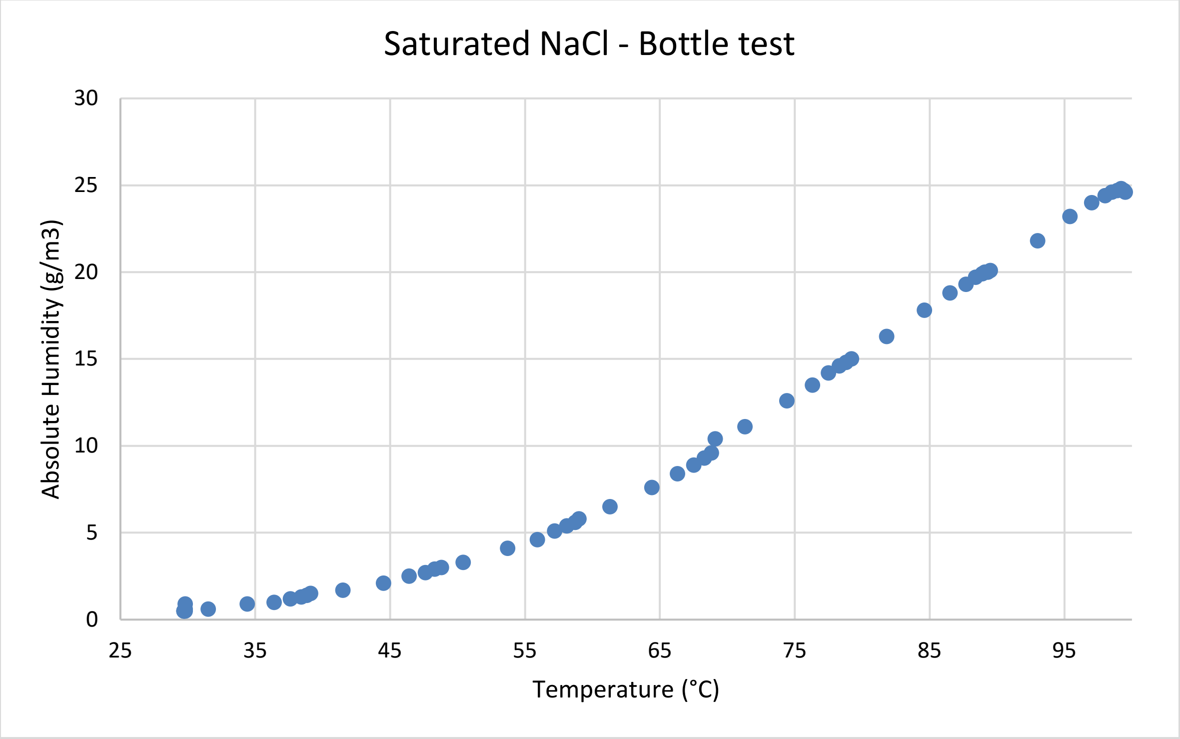

Figure 17. Bottle humidity measurements as a function of temperature from the saturated sodium chloride solution headspace.

Finally, the Teflon-lined sample bottles from the saturated sodium chloride test were tested, the bottle fill humidity readings shown in Figure 12 and Figure 13. The bottle test results are shown in Figure 18 and Figure 19. The absolute humidity readings from the first bottle at 100°C (28.1 g/m^3) are much greater than the final reading taken in the assembly above the sample bottle (21.8 g/m^3). The first bottle showed a slight 'jump' in absolute humidity at approximately 50°C, this is likely within the error of the probe.The absolute humidity readings from the second bottle at 100°C (28.9 g/m^3) are much greater than the final reading taken in the assembly above the sample bottle (21.6 g/m^3). The second bottle measurement had an extended hold time which is the rise in humidity readings at approximately 50°C. Additionally, the two tests are in good agreement with one another indicating the possibility of good replication of results.

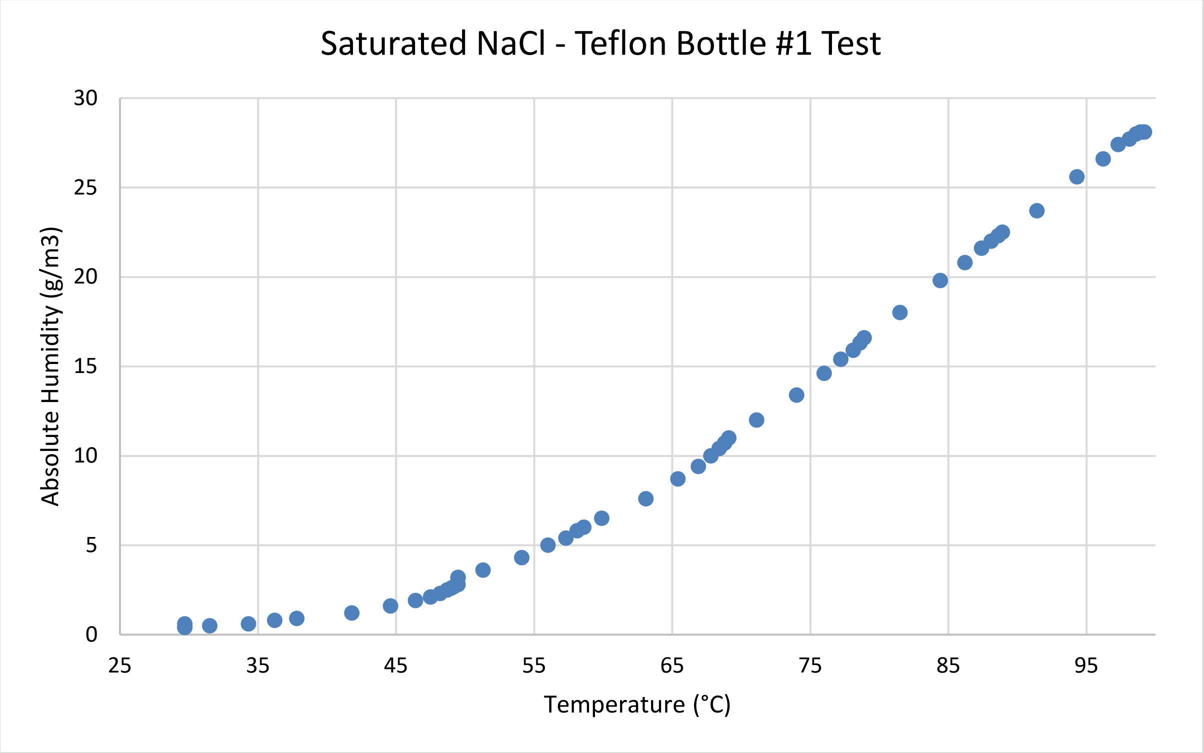

Figure 18. Teflon-lined bottle humidity measurements as a function of temperature from the saturated sodium chloride solution headspace.

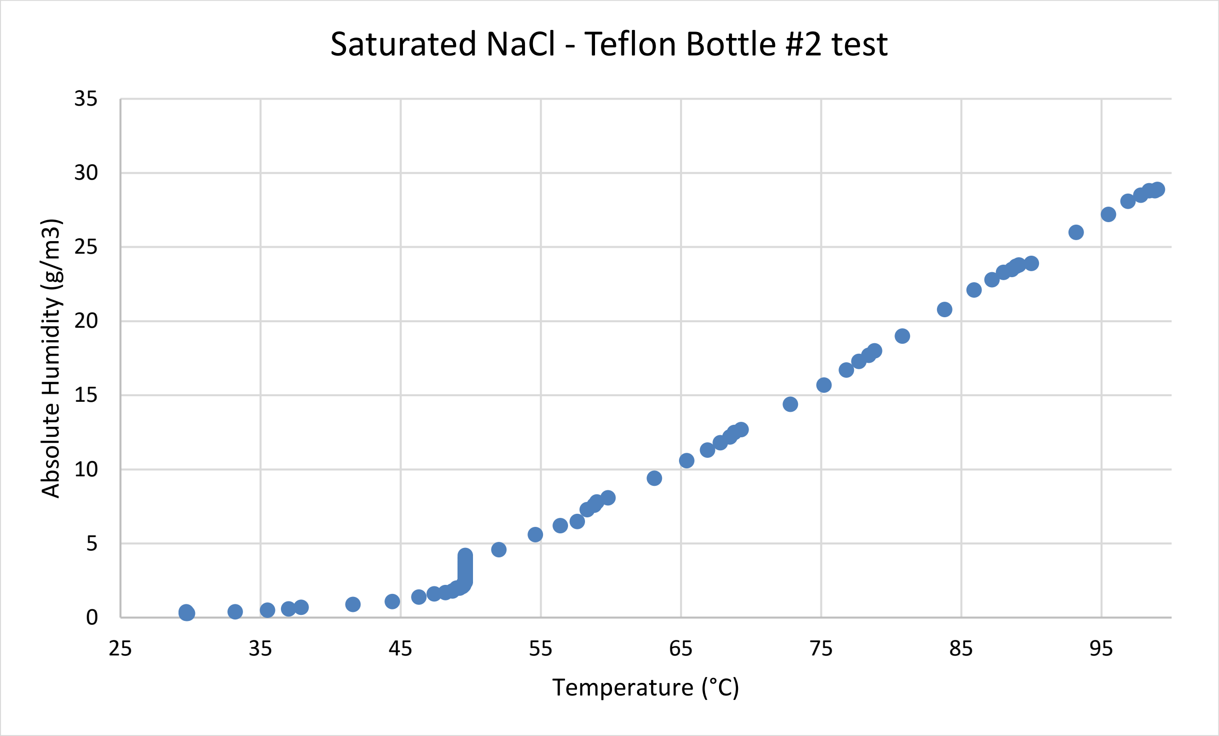

Figure 19. Teflon-lined bottle humidity measurements as a function of temperature from the saturated sodium chloride solution headspace.

3.3 Test C – Surface Drying Tests

For these tests, the amount of water desorbed from the surface of cladding material will be measured gravimetrically over a temperature range consistent with measurements made in the HBDP cask during vacuum drying. Based on the expected mass loss for a range of water surface concentration for 0.375-in., outer-diameter tubing at different lengths, 7-in. length of tubing was selected to expose the inner and outer surfaces of the cladding. These tests are ongoing.

The samples are oxidized in an autoclave and placed in a water bath to saturate the surface. The samples are then placed in a drying oven and held at stepwise increasing temperatures. Sample masses are measured and recorded periodically to determine when drying at a temperature is complete. Use of a thermogravimetric analysis system was considered for this test but these systems require a small sample mass with a large surface area. Metal powders could be used with this type of approach but would not be representative of the bulk cladding materials. Consequently, the approach described in this section will be attempted despite the challenge of measuring small mass differences of large cladding tube segments.

3.3.1 Key Test Details

The key test equipment for this test are described below:

- A micrometer capable of measuring specimen dimensions to 0.002 in. (0.05 mm)
- A balance capable of weighing specimens to 0.1 mg and capacity of 25 g
- An autoclave capable of achieving a temperature of 360°C
- A drying oven capable of heating to 300°C, and 7-in. lengths of cladding.

Four types of cladding tubes will be tested—three PWR tube types and one boiling water reactor (BWR) tube type. Some of the cladding alloys are consistent with the cladding loaded in the demo cask. Six samples for each of four cladding tube types will be tested. Prior to autoclaving each cladding, samples were measured for length, diameter, thickness, and mass. This step is complete.

The cladding tubes are being staged for autoclave oxidation of the surface using simulated reactor water, which has approximately 1000 ppm H_3BO_3 and 2 ppm LiOH. The autoclave is operated at 360°C for 72 hours. After autoclaving, each cladding sample will be re-measured to determine the impact of oxidation on cladding dimensions and mass . The samples will then be placed in a water bath at 60°C for 1 week to hydrate the oxide layer and ensure adsorbed water equilibrium. At the end of the week, the samples will be air-dried at ambient temperature and then re-measured again for length, diameter, thickness, and mass.

Next, the cladding samples will be placed in a drying oven to gravimetrically determine the amount of physiosorbed water on the samples using an analytical balance. The daily mass of each sample will be recorded until the samples reach constant mass (there is less than 1% change in mass loss over a 24-hour period) at each temperature. The samples will be placed in a desiccator to cool prior to weighing. This will occur at three different oven set points—150°C, 200°C, and 250°C. The samples then will be cooled to ambient temperature, and their lengths, diameters, and thicknesses will be measured to obtain the nominal bulk surface area. The mass loss-to-surface area ratio for each sample at each temperature will then be calculated.

To date, about half of the cladding samples required for all testing have been processed through the autoclave. To help alleviate future bottleneck issues with autoclave operations, a second system has been ordered from Parr. The new system is shown in the rendering from the vendor in Figure 20. The new system is scheduled to be delivered and installed in the last quarter of FY2021.

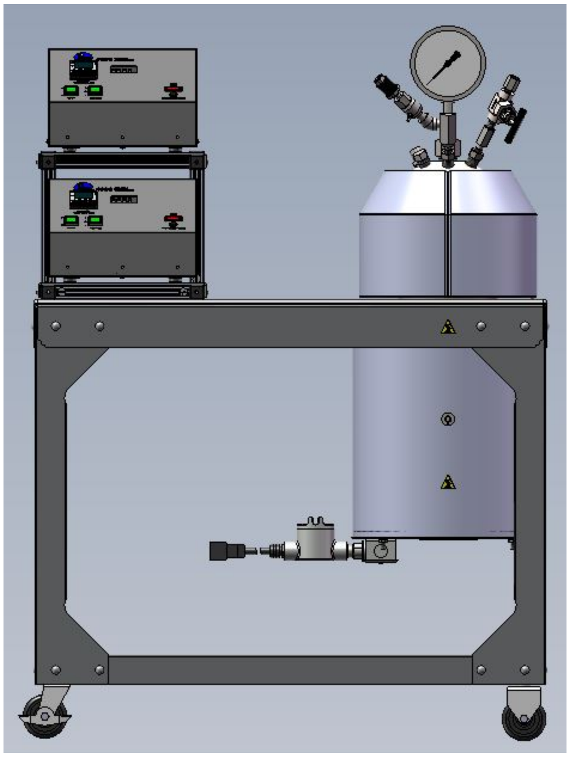

Figure 20. Vendor rendering of new autoclave system.

3.4 Test D – Small-Scale Drying of Cladding

For this test series, the cladding array will initially be oxidized and saturated with water or simulated spent fuel pool water to study the humidification of the backfill gas from cladding surface water desorption. This desorption will be studied before and after vacuum drying at a temperature consistent with measurements made on the HBDP cask during vacuum drying. Four different conditions are planned to be tested. Two conditions correspond to the cladding tubes being placed in a bath of DIW prior to testing and the other condition will use a bath of simulated pool water (i.e., DIW with 2500 ppm boron [14,300 ppm H_3BO_3]). The purpose of these tests is to see if boric acid deposits on the surface of the cladding lead to increases in humidity as postulated by Bryan et al. (Bryan, et al., 2019). Two additional conditions will test the influence of the vacuum drying by performing rebound tests (by evacuating the pressure vessel and observing the pressure change over time) with and without applying vacuum drying in a manner consistent with the HBDP approach. These test conditions are summarized in Table 1.

Table 1. Test Matrix for Test D

Test ID#	Water Bath Solution	Vacuum Drying Hold Time (hr)	Vacuum Drying Hold Point (Torr)	Rebound Test Hold Time (min)	Rebound Test Starting Pressure (Torr)
D1	DIW	n/a	n/a	30	0.4
D2	DIW	7	10	30	0.4
D3	DIW with 2500 ppm boron (14,300 ppm H_3BO_3)	n/a	n/a	30	0.4
D4	DIW with 2500 ppm boron (14,300 ppm H_3BO_3)	7	10	30	0.4

These data will be compared to the HBDP data to investigate the contribution of cladding and boric acid deposits on the water vapor in the gas samples. The test is designed to isolate the effects of the cladding on the headspace of the vessel and does not account for thermal similitude of the full-scale system. These aspects will be tested by SNL in a future effort discussed by Salazar et al. (Salazar, Pulido, Lindgren, & Durbin, 2020).

Bryan et al. (Bryan, et al., 2019) report that crud on the cladding could be a significant source of water vapor. The test described in this section focuses on clean and oxidized cladding. Future tests could focus on growing simulated crud on the cladding tubes. Lin (Lin, 2014) provides a procedure for producing simulated crud that could be adapted to for this test. Cladding with crud deposits could then be tested to investigate this potential source of water vapor. Additionally, thermogravimetric tests could be performed on the simulated crud to study the behavior of these materials in greater detail.

The test system shown in Figure 7 will be used for this test. Instead of a salt solution, an array of cladding materials will be used in the arrangement similar to what is shown in Figure 21. This arrangement consists of 45 cladding tubes that are 7 in. long. The tubes will be open so both the inner and outer surfaces will be potential water vapor sources. The basis for this design decision is to maintain a similar gas volume-to-cladding surface ratio between the full-scale and small-scale systems. This ratio is an important parameter for assessing the cladding as a potential water vapor source. For this configuration, the gas volume-to-cladding nominal surface area ratio is 0.67 cm. For a full-scale cask, the ratio is ~0.66 cm. The anticipated amount of water added to the system through the addition of the hydrated layers on cladding will be calculated to determine if the contribution to the vessel headspace humidity will be measurable using the Vaisala humidity probe. This calculation will also inform the feasibility of performing liquid isotopic measurements to trace humidity in the system.

Figure 21. Cladding lengths that have undergone oxidation in the autoclave.

First, the 7-in cladding tubes will be oxidized by autoclaving. Four types of cladding tubes will be tested—three PWR tube types and one BWR tube type. Some of the cladding alloys are consistent with the HBDP cask. Four sets of 45 tubes, one of each cladding tube type are needed for the test. The cladding tubes will be autoclaved to oxidize the surface using simulated reactor water, which has approximately 1000 ppm H_3BO_3 and 2 ppm LiOH. The autoclave will operate at 360°C for 72 hours. After autoclaving, each cladding sample will be measured for length, diameter, thickness and mass. The cladding samples will then be placed in a water bath at 60°C for 1 week.

The next step is to precondition the pressure vessel and tube holders. The 1-gallon pressure vessel, sensors and data acquisition system described in Section 3.1.1 will be used for the testing in the Fisher IsoTemp oven which is large enough to accommodate the apparatus. This will be accomplished by loading the tube holder into the pressure vessel and placing the vessel in the oven. Next, the oven will be set at 90-100°C for 16–24 hours. During this time, the pressure vessel will be evacuated to mid-to-high vacuum levels (nominally in the milli-Torr range).

Next, the pressure vessel will be opened, and cladding tubes will be pulled from the water bath and placed in the tube holder while still wet. The vessel will be sealed and the data acquisition system started. The oven will be set to 140°C. When the thermocouples in the pressure vessel reach thermal steady state, a vacuum will be applied to achieve a target absolute pressure specified in Table 1. When vacuum drying is required, the system will be pumped down to a target pressure is 10 Torr with a hold time of 7 hours. These steps will be performed while the data acquisition system is running.

For the rebound test, the target starting pressure is 0.4 Torr. If the target pressure cannot be achieved, the starting pressure will be the lowest stable pressure achievable. The pressure vessel will then be isolated from the vacuum pump from system, and data will be recorded for 30 minutes. Next, the pressure vessel will be backfilled with 2.2 bar He while at 140°C, and the final steady-state humidity level will be measured. Data will be recorded for 2 weeks or until the humidity levels have stabilized to <1% difference over 24 hours.

Subsequent tests will be initiated by placing the cladding tubes back into the water bath at 60°C for 1 week. The bath solution will consist of DIW and simulated pool water with 2500 ppm boron (14,300 ppm H_3BO_3). Transient humidity levels for all test conditions will be plotted to see if any match the linear profile shown in the demo cask. In addition, the final humidity level in the system will be compared to the actual cask measurements.

3.5 Test E – Small-Scale Drying of Guide-Tube/Dashpots

For this test series, the contribution of humidity to the backfill gas from water accumulated in commercial guide-tube and dashpot assemblies will be studied before and after vacuum drying at a temperature consistent with measurements made on the HBDP cask during vacuum drying. The guide-tube and/or dashpot assembly will be initially filled with a test solution. Four different conditions will be tested. Two conditions correspond to the test materials being filled with DIW prior to testing and the other condition will fill the test materials with simulated pool water consisting of DIW with 2500 ppm boron (14,300 ppm H_3BO_3). The purpose of these tests are to see if boric acid deposits on the interior surface of the materials will lead to increases in humidity as postulated by Bryan et al. (Bryan, et al., 2019) or if the drain holes will be obstructed due to these deposits. Two additional conditions will test the influence of the vacuum drying by performing rebound tests with and without applying vacuum drying in a manner consistent with the HBDP approach. These test conditions are summarized in Table 2.

Table 2. Test Matrix for Test E

Test ID#	Water Bath Solution	Vacuum Drying Hold Time (hr)	Vacuum Drying Hold Point (Torr)	Drying Criteria Hold Time (min)	Drying Criteria Starting Pressure (Torr)
E1	DIW	n/a	n/a	30	0.4
E2	DIW	7	10	30	0.4
E3	DIW with 2500 ppm boron (14,300 ppm H_3BO_3)	n/a	n/a	30	0.4
E4	DIW with 2500 ppm boron (14,300 ppm H_3BO_3)	7	10	30	0.4

These data will be compared to the HBDP data to investigate the contribution of guide-tube/dashpots and boric acid deposits on the water vapor in the gas samples. The test is designed to isolate the effects of the guide-tube/dashpots on the headspace of the vessel and does not account for thermal similitude of the full-scale system. These aspects will be tested by SNL in a future effort discussed by Salazar et al. (Salazar, Pulido, Lindgren, & Durbin, 2020).

With the exception of the pressure vessel, the system components from Test D will be used for the testing. To accommodate the height of the guide-tube sections and dashpot assemblies, a larger pressure vessel is required. The pressure vessel selected is manufactured by Alloy Products Corporation out of 316L stainless steel with a 4-gallon capacity and is American Society of Mechanical Engineers stamped with a rating full vacuum to 132 psig at 150°C. The next step is to precondition the pressure vessel and test materials. This will be accomplished by loading the test materials into the pressure vessel and placing the vessel in the oven. Next, the oven will be set at 90-100°C for 16–24 hours. During this time, the pressure vessel will be evacuated mid-to-high vacuum levels (nominally in the milli-Torr range). The use of cartridge heaters in place of the oven for better simulation of the process is being explored. Should they be used, the test will not be executed exactly as detailed below.

After the vessel cools, the test materials will be filled to the lower drain hole with a solution consistent with Table 2. The solution will consist of both DIW and simulated pool water with 2500 ppm boron (14,300 ppm H3BO3). Next, the pressure vessel will be opened, and the guide-tube/dashpot mockup will be placed in the pressure vessel. The vessel will be sealed and the data acquisition system started. The oven will be set to 140°C. When the thermocouples in the pressure vessel reach thermal steady state, a vacuum will be applied to achieve a target absolute pressure specified in Table 2. When vacuum drying is required, the system will be pumped down to a target pressure of 10 Torr with a hold time of 7 hours. These steps will be performed while the data acquisition system is running.

For the rebound test, the target starting pressure is 0.4 Torr. If the target starting pressure is not achievable, the lowest stable vacuum level will be used. The pressure vessel will then be isolated from the vacuum pump and data recorded for 30 minutes. Next, the pressure vessel will be backfilled with 2.2 bar He while at 140°C, and then final steady-state humidity level will be measured. Data will be recorded for 2 weeks or until the humidity levels have stabilized. After cooling, the test materials will be inspected visually and gravimetrically, if possible, for the presence of any free liquid.

Transient humidity levels for all test conditions will be plotted to see if any match the linear profile observed in the demo cask. In addition, the final humidity level in the system will be compared to the actual cask measurements.

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4. SUMMARY

This report documents the interim testing status of the small-scale drying testing at PNNL. These small-scale drying tests are to develop the technical bases for sensors, techniques, and approaches that will be used to address the challenges faced when determining moisture content from gas samples from spent nuclear fuel canisters. Specifically, the purpose of these tests is to support SNL gas sample methods and analyses through a series of five small-scale experiments as summarized in section 3. Current status and summary are as follows:

- *Test A, Method Development and Sample Bottle Loading* – The sample bottle humidity level does not match the vessel headspace, however, with enough data a look-up table or correlation function could be derived. During FY2021, extended bottle loading times were tested to determine if the bottle would reach equilibrium given enough time. For a saturated headspace, an offset of 4 g/m^3 absolute humidity between the vessel headspace and the humidity probe above the sample bottle remained. When the surface area was reduced by replacing the sample bottle with tubing, the offset between the probes dropped to 3 g/m^3. For an approximately 75% RH condition using a sodium chloride solution, the probes came to near agreement, at least within the error of the probes. The Vaisala probes in both vertical and horizontal configuration with different humidity conditions will be repeated with the new pressure vessel that allows for both vertical and horizontal configuration.
- *Test B, Sample Bottle Measurements* – The sample bottles collected in the extended bottle fill testing in FY2021 gave humidity readings at 100°C that are greater than the measured humidity when they are filled at 30°C. The bottle data can be correlated to the original humidity of the vessel given enough data. Based on the observations from these tests, additional testing is warranted to better understand the behavior of the readings with different test temperatures, hold times, and surface areas of the probe portion of the system.
- *Test C, Surface Drying Tests* – Autoclave oxidation of cladding is ongoing. Once oxidation of materials is complete, this test can be executed.
- *Test D, Small-Scale Drying of Cladding* – Autoclave oxidation of cladding is ongoing. Once oxidation of materials is complete, this test can be executed.
- *Test E, Small-Scale Drying of Guide-Tube/Dashpots* – Rather than using the previously fabricated mockup assembly (see FY2020 report (Colburn, 2020)), commercial guide tube material and dashpots are being procured for testing.

The COVID-19 pandemic has had a significant impact on this project presenting supply chain issues that have significantly delayed planned experimental activities. As more data becomes available, PNNL will reach out to SNL for collaboration on this work. .

4.1 Future Work

4.1.1 Overall

- Build a duplicate data acquisition system to improve efficiency in completing testing, this could be accomplished in early FY2022.
- Explore changing the thermocouples to T-type thermocouples to improve the system precision. This could be accomplished in FY2022 while the data acquisition system is taken out of service for calibrations.
- Complete installation and commissioning of the autoclave system for cladding and fuel assembly oxidation. Complete the oxidation of cladding for the planned Tests C and D as described in section 3 by January 2022.

4.1.2 Test A, Method Development and Sample Bottle Loading

- Verify the Vaisala probe performance in known humidity conditions. Using the new pressure vessel with two probes, one mounted horizontally, one vertically the same conditions previously tested in FY2020 will be used. Perform an error propagation to better inform the uncertainty in the measurements using the Vaisala variable capacitance probes. This will be completed by end of Q1 of FY2022.

4.1.3 Test B, Sample Bottle Measurements

- In order to correlate conditions in the pressure vessel to those in the sample bottles, a detailed test plan will be derived for testing to determine either a mathematical relationship or a ‘look-up’ table for use in the future. PNNL acknowledges that many variables will need to be considered in this study such as temperature, hold times, surface area of the assembly as well as surface material of the test assembly and the sample bottles. PNNL will be seeking input from SNL for this activity. PNNL intends to begin working on this test plan in FY2022 and to begin executing this work if an additional data acquisition system is built to allow for concurrent testing.

4.1.4 Test C, Surface Drying Tests

- Complete the planned gravimetric testing by the end of Q2 FY2022
- Explore getting BET surface area of the oxidized cladding before and after drying.
- Explore conducting testing with powdered materials and compare results after normalization of the surface area to the oxide layers on cladding

4.1.5 Test D, Small-Scale Drying of Cladding

- Explore the use of cartridge heaters to heat the cladding from the inside to be more prototypic of the process in the spent fuel cask.
- Explore getting BET surface area of the oxidized cladding before and after drying.
- Explore conducting testing with powdered materials and compare results after normalization of the surface area to the oxide layers on cladding

4.1.6 Test E, Small-Scale Drying of Guide-Tube/Dashpots

- Work with project staff to acquire PWR and BWR fuel assembly pieces that are suspected of water retention
- Explore the use of cartridge heaters to heat the guide tubes and dashpot hardware from the inside to be more prototypic of the process in the spent fuel cask.
- Work with SNL to test materials provided to provide feedback to the large scale testing.

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