Small-Scale Drying: FY2020 Interim Report

Spent Fuel and Waste Disposition

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EXECUTIVE SUMMARY

This report documents the interim experimental status of small-scale drying tests currently being performed at Pacific Northwest National Laboratory. 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 taken at the North Anna Nuclear Generating Station for the High Burnup Demonstration Project. 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 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 this report outlines a series of five tests and any data collected to date that were planned for FY 2020 that 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. This interim report documents the experimental background, design and progress of these small-scale drying tests. Further data gathered will be summarized in the FY 2021 report.

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REVISION HISTORY

REVISION	COMMENTS	ISSUE DATE
A	Initial draft for PNNL Information Release	7/27/2020
0	Final Version for Release	8/21/2020

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ACRONYMS

BWR	boiling water reactor
DIW	deionized water
DOE	US Department of Energy
EPRI	Electric Power Research Institute
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 (%)
SNF	spent nuclear fuel
SNL	Sandia National Laboratories

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SMALL-SCALE DRYING – FY 2020 INTERIM REPORT

1. INTRODUCTION

In an effort to better understand the properties of high burnup spent nuclear fuel (SNF) during storage and transportation, the Department of Energy Office of Nuclear Energy and the Electric Power Research Institute (EPRI) created a cooperative research program. The program is focused on collecting data from a SNF dry storage system containing high burnup fuel. As EPRI explains in their test plan (EPRI 2014), the collected data are designed to be most relevant to high burnup fuel in dry storage by closely mimicking the real conditions high burnup SNF experiences during all stages of dry storage, such as, loading, cask drying, inert gas backfilling, and transfer for storage.

This multi-year program is in progress and Bryan et al. (2019b) explains that in November of 2017, the cask for the High Burnup Demonstration Project (HBDP) was filled with fuel from the spent fuel pool at the North Anna Nuclear Generating Station. Table 1 shows a breakdown of the cladding types in the cask.

Table 1. Quantities of HBDP Cladding Types

Clad Type	Quantity	Burnup Range (GWd/MTU)
Zr-4	1	50.6
Low tin Zr-4	1	50
Zirlo	12	51.9–55.5
M5	18	50.5–53.5

After the fuel was loaded, a vacuum drying method was used in which the water was siphoned from the cask, and then a vacuum was pulled on the cask, which caused the cask temperature to increase to above-boiling temperatures. The vacuum drying period lasted approximately 7 hours. When the procedure was complete, 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—presumably water evaporation or desorption—within the cask. The acceptance criterion is that the pressure remains below 4 mbar (3 Torr) after 30 minutes (Jung, et al., 2013). Figure 1 shows the transient pressure data from this test. The behavior of the pressure increase 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). There is also the possibility of ice formation during vacuum drying and diffusion of liquid water from crevices and pockets in the bulk volume of the cask. Therefore, the interpretation of these data may not be solely attributed to water desorption.

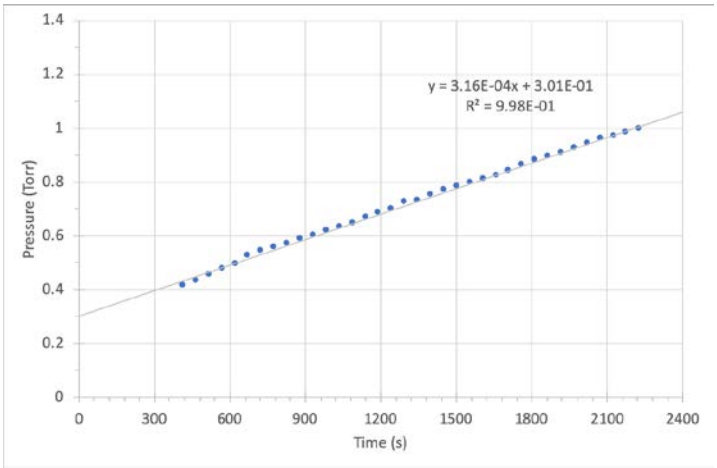

Figure 1. 30-minute Rebound Test Data for the HBDP Cask (from EPRI 2019)

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.

The first set of three samples was analyzed by Dominion Energy at the North Anna site, using a water vapor isotope analyzer from Los Gatos Research (EPRI 2019). The second set of three samples were analyzed at Sandia National Laboratories (SNL) using two types of hygrometers. The primary SNL hygrometer was a Vaisala relative humidity probe (Model HMP77B, relative humidity 0% to 100%, −70°C to 180°C). The Vaisala probe is a high-quality variable capacitance probe. SNL reports that, as with other probes of this type, it is quite accurate at high relative humidity values, but progressively less so at lower values (Bryan et al. 2019b). A second chilled mirror hygrometer, which has high accuracy but requires gas flow over the mirrors, was also used. A summary of the results of these analyses is shown in Table 2. With the exception of the Dominion Energy measurements, the water content measurements show increasing humidity over the 12-day sampling period. Note that the Dominion sample results were adjusted 10–20% downward on the basis of a separate measurement of a gas standard supplied by SNL (Bryan et al. 2019b). Also, Bryan et al. (2019b) report that due to difficulties with a chilled mirror hydrometer gas flow system, the SNL hygrometer data for samples 1 and 2 are considered compromised and therefore only estimates are reported. Sample 3 of Table 2 below is considered to have the most reliable data set.

Table 2. Summary of Water Vapor Measurement Results (ppmv) from HBDP Cask Samples

Sample #	Time (hr)	Total Time (min)	Dominion Energy (ambient)	SNL Hygrometer (ambient 23ºC)	SNL Hygrometer (65ºC)
1	5 hours after He backfill	~300	2,000-2,100	~2,097 (compromised)	no data
2	5 days after sample 1	~7,500	8,896	~6,600 (compromised)	~10,000 (compromised)
3	7 days after sample 2	~17,580	8,300	11,200 @ 29 psia	17,400 @ 33 psia

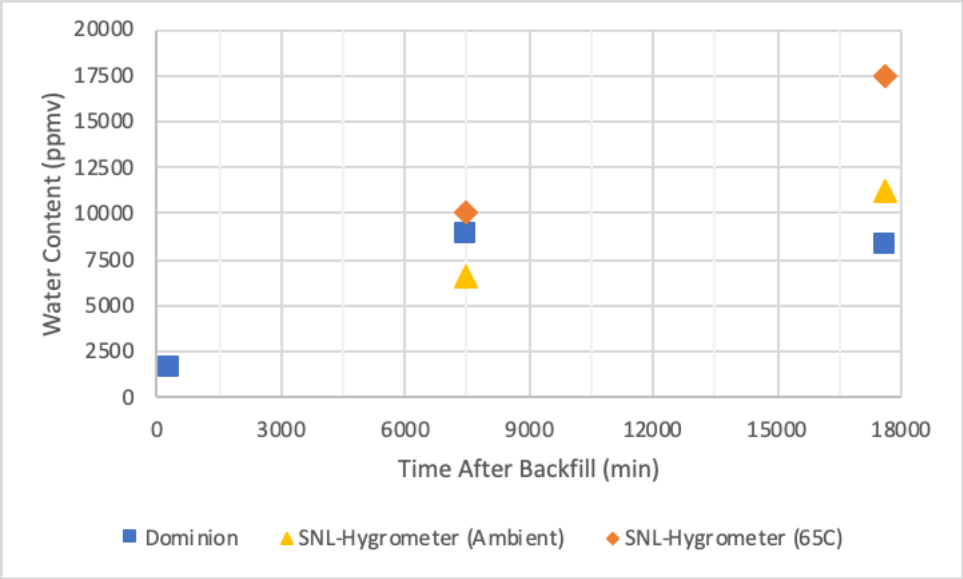

Figure 2. Summary of Water Content Measurements at Various Times after Backfilling (from Bryan et al. 2019b)

Focusing on the sample 3 data, the interior sample bottle surface area is estimated at approximately 762 cm^2 with a capacity of 1 L. At 23°C and a pressure of 29 psia, the initial molar quantity of gas in the bottle can be calculated from the ideal gas law as 80.2 mmol. At 65°C and a pressure of 33 psia, the quantity of gas is estimated at 79.5 mmol. There is also a 6200 ppmv difference in water concentration between the ambient temperature (23°C) and 65°C conditions. Using these values, Equation (1) can be used to estimate the quantity of water that was liberated in the bottle. The calculation results in about 9 mg of water vapor generated between 23°C and 65°C in the 1-L bottle. Based on this calculation, the surface concentration of water vapor would be about 12 µg/cm^2. For comparison, Kochsiek (1982) reports that sorbed water content on stainless steel is typically less than 1 µg/cm^2 (Table 3). The SNL results indicate about an order of magnitude higher than the literature values.

$$n_{65} - n_{23} = \left(\frac{x_{65}}{1-x_{65}} - \frac{x_{23}}{1-x_{23}}\right) n_0 \quad (1)$$

where: n_{65} is the number of moles of water at 65°C

n_{23} is the number of moles of water at 23°C

x_{65} is the mole fraction of water at 65°C (0.0174 from Table 2)

x_{23} is the mole fraction of water at 23°C (0.0112 from Table 2)

n_o is the initial number of moles of gas in the sample bottle.

Table 3. Typical Water Concentration of Stainless Steel (15% Ni, 20% Cr) Surfaces (Kocksiek 1982)

Description	Mass Coverage (µg/cm^2)
Ground surface electrolytic	0.4-0.7
Polished surface	0.25-0.3

There could be several reasons for this difference including: (1) the surface area of the sample bottles were much larger than our estimates, (2) a component in the SNL system was not completely dewatered during pretreatment at elevated temperature and under vacuum, or (3) the estimate from Kochsiek (1982) was not directly applicable to the sample bottle. Interestingly, the SNL report (Bryan et al. 2019b) describes efforts to assess the uncertainty of the Vaisala HMP77B sensor with a purchased humidity standard and reported good agreement (~5% low) at 25°C. They reported that gas increased markedly as the temperature rose, with the concentration at 60°C more than double the concentration at 25°C. Unlike the HBDP cask samples, the standard showed a near linear increase of humidity with temperature and was not leveling out over the temperature range measured.

Bryan et al. (2019a) 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. (2019a) 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 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 (2018) provides measured cask temperatures through the HBDP cask drying process for cells 14 and 28 in Figure 1 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. (2019a) 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. TEST PURPOSE

The purpose of this test is to support 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. (2019a) that can contribute to the presence of water vapor
- Assess the accuracy of the hygrometer used to measure sample 3 (Vaisala probe) under a wider array of temperatures, water vapor concentrations, and gas environments than the initial Bryan et al. (2019b) validation tests.
- Identify additional methods for measuring humidity in cask easily and accurately using lessons-learned from the Bryan et al. (2019b) report including direct gravimetric and isotopic tracer techniques.

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3. TEST OBJECTIVES

There are two main objectives to this test. 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 from sorption layers on the cladding material?
- 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)? It is believed that crud would contribute water to the system in a similar way to the oxide layers on cladding.

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4. TEST APPROACH AND INTERIM RESULTS

Five tests, designated Tests A–E, were developed and are in progress to support the test purpose and objectives. They are described in more detail in the following subsections. 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 SNL sample 3 humidity results.
- *Test B, Sample Bottle Measurements* – The purpose is to increase confidence in the sampling measurement approach used by SNL for the sample 3 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. Additionally, the test will employ lessons-learned documented by Bryan et al. (2019b) for using an isotopic tracer and gravimetric measurements as alternative approaches for water vapor measurements from the gas samples.
- *Test C, Surface Drying Tests* – The purpose is to measure the amount of water desorbed from the surface of 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 the contribution to the backfill gas from water desorbed 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 the contribution to the backfill gas 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.

4.1 Test A – Method Development and Sample Bottle Loading

This test series was designed to increase confidence in the sampling and measurement sensor technology used for the SNL sample 3 humidity results. The tests covered a range of relative humidity values using a set of saturated salt solutions. The saturated salt solutions were controlled over a range of temperatures just below the boiling point. The salt solutions had a helium cover gas at pressures ranging from 1–8 bar. The salt solutions were also measured with air as the cover gas. These conditions provided a range of controlled relative humidity environments that were measured with a Vaisala probe model HMP4, which employs similar variable capacitance sensor technology to the Vaisala HMP77B sensor used by SNL. The HMP4 is designed for industrial process applications and has an operating temperature range of −70°C to 180°C, relative humidity measurement range of 0% to 100%, and an operating pressure range of 0 to 100 bar. This sensor is the same class of humidity sensor but has improved accuracy and response time compared to the Vaisala HMP77B sensor used by SNL.

Additional humidity sensor types were assessed but not selected for further study. These included 1) a chilled mirror system produced by RH Systems LLC (Model 473), and 2) a tunable laser absorption spectroscopy system produced by NEO Monitors (Model LaserGas II). The chilled mirror system requires a complicated flow loop system to achieve gas flow over the mirror, which presented a challenge to SNL. It is also not compatible with the helium cover gas used. The tunable laser absorption spectroscopy system had minimum pressure and path length requirements for accurate measurements. For these reasons, the variable capacitance sensor technology used by Vaisala was considered the most promising for further study.

The tests also replicated the gas sampling process by taking samples into sample bottles (pretreated to remove initial residual water) that were cooled to ambient temperature and stored. The bottles are reheated, as discussed in Test B. A second set of hygrometer measurements were taken from the heated

sample bottles for comparison to the controlled environment measurements. Initially, only six of the tests at 2.2 bar were sampled. Duplicate and triplicate samples were taken. Photographs of the actual system are shown in Figure 3.

Figure 4 shows the vapor pressure of several saturated salt solutions over a range of temperatures from data with uncertainty ranges provided by Greenspan (1977). From these data, a matrix of test temperatures and salt compounds for testing was selected. To cover the range of conditions corresponding to sample 3, deionized water (DIW) and four salt solutions—NaCl, LiBr, LiCl, and NaI—were selected at temperatures of 30°C, 65°C, and 90°C and pressures of 1 bar, 2.2 bar, and 8 bar. Cover gases included air and helium.

The complete test matrix is shown in Table 4. This design resulted in 36 distinct tests to assess hygrometer performance—12 tests with four different liquids. To minimize the number of gas sample analyses and replicate the gas sampling conditions for the HBDP, samples were only taken for some of the tests at pressures of 2.2 bar. Because samples were taken in triplicate, a total of 18 samples were taken at six distinct conditions which are shown in bold in Table 4.

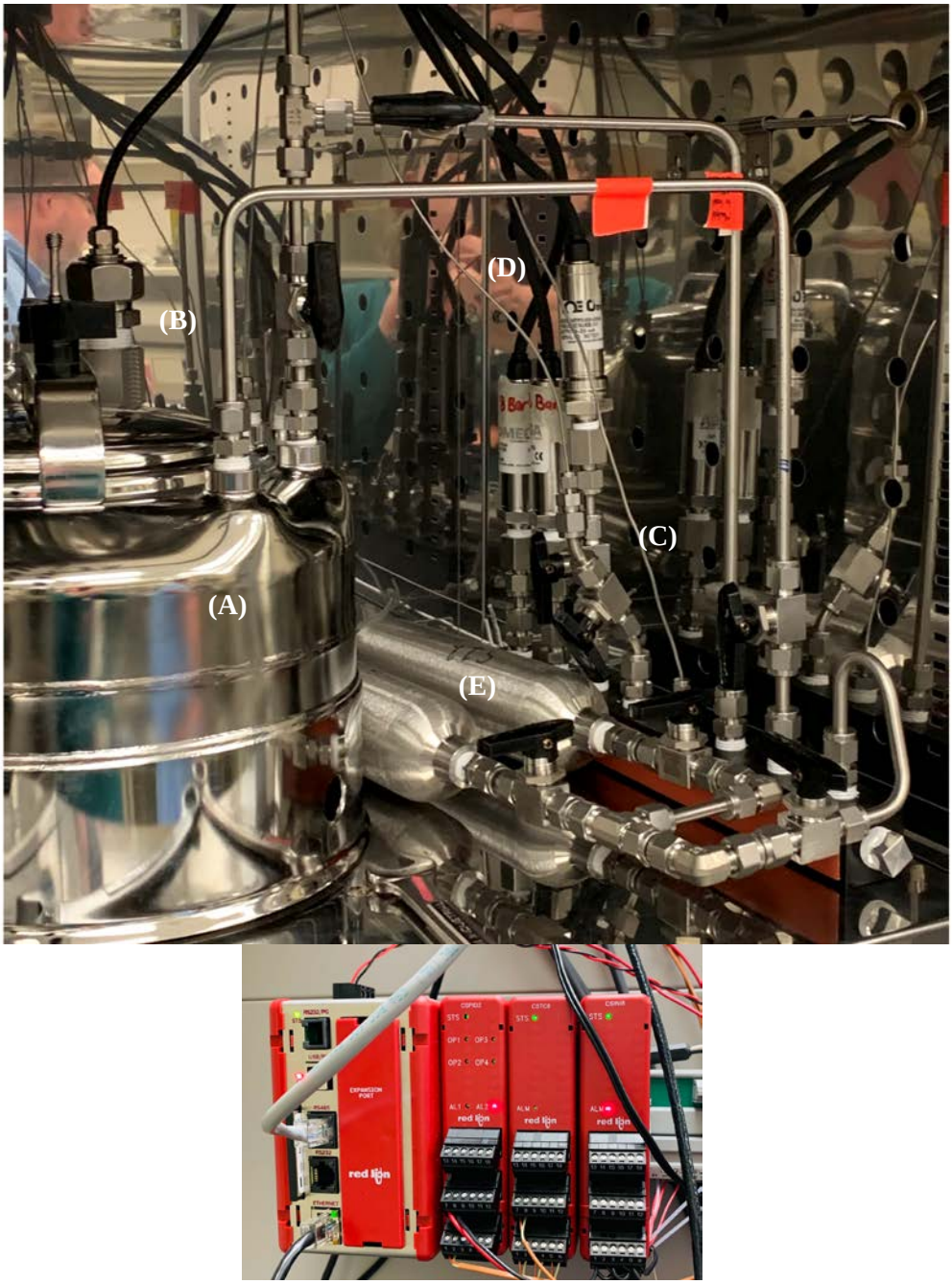


Figure 3. Top: Photo of Test Apparatus for Tests A, D, and E. Pressure vessel (A) in oven with Vaisala humidity sensor mounted vertically in the vessel headspace (B). Instrument manifold housing thermocouples (C), pressure transducers (D). Sample bottles installed (E). Bottom: Photograph of data acquisition system.

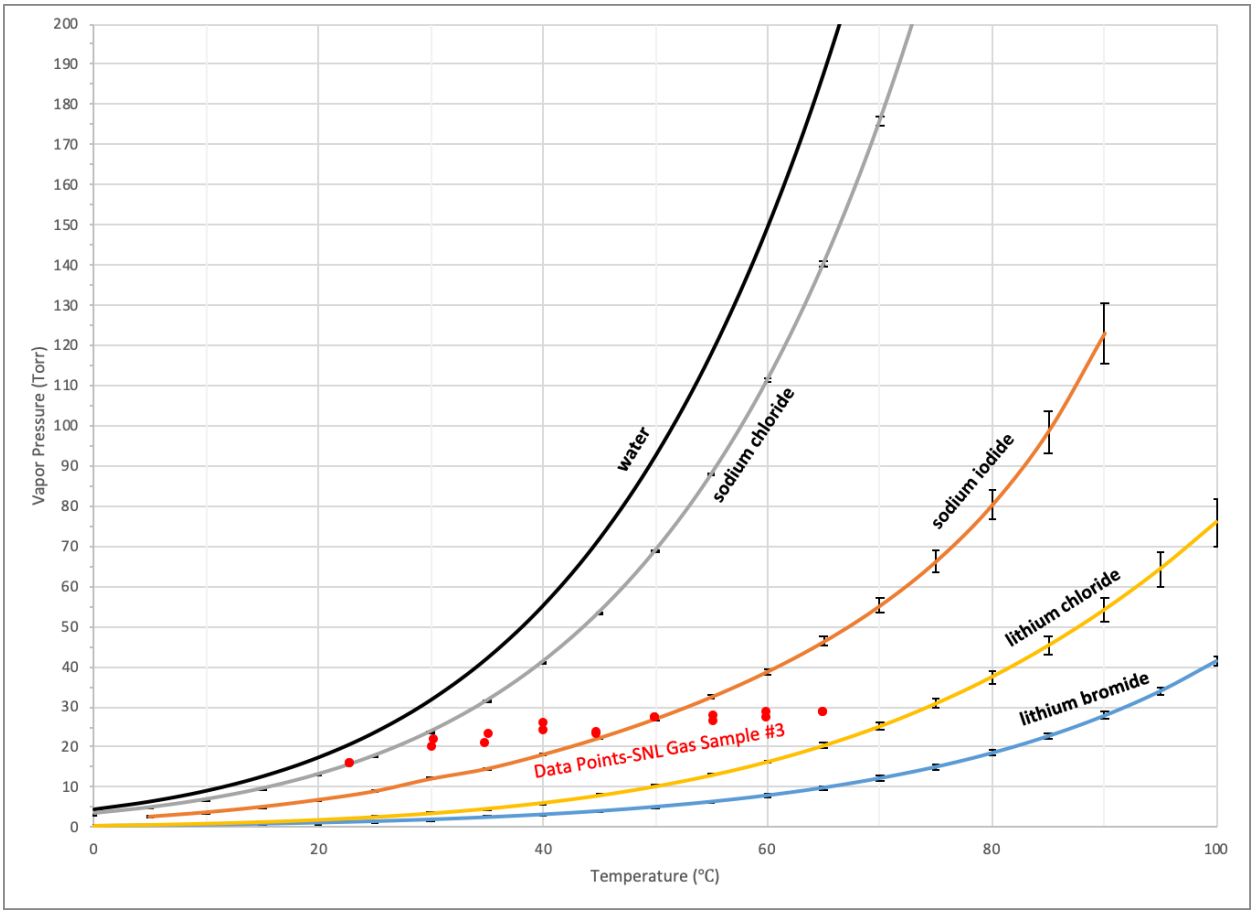


Figure 4. Vapor Pressure of Saturated Salt Solutions Used for Test A

Table 4. Test Matrix for Tests A – Method Development and Sample Bottle Loading

Test	Gas	P (bar)	T (°C)	Source Liquid	Relative Humidity (%)	Vapor Pressure (Torr)	Water Concentration (ppmv)
A1	Air	1	30	DIW	100	31.8	44354
A2	He	1	30	DIW	100	31.8	44354
A3	**He**	**2.2**	**30**	**DIW**	**100**	**31.8**	**19685**
A4	He	8	30	DIW	100	31.8	5337
A5	Air	1	30	NaCl	75	23.9	32901
A6	He	1	30	NaCl	75	23.9	32901
A7	**He**	**2.2**	**30**	**NaCl**	**75**	**23.9**	**14691**
A8	He	8	30	NaCl	75	23.9	3997
A9	Air	1	30	NaI	36	11.5	15527
A10	Air	1	65	NaI	25	47.0	66789
A11	Air	1	90	NaI	23	121.1	192490
A12	He	1	30	NaI	36	11.5	15527
A13	He	2.2	30	NaI	36	11.5	6998
A14	He	8	30	NaI	36	11.5	1915
A15	He	1	65	NaI	25	47.0	66789
A16	**He**	**2.2**	**65**	**NaI**	**25**	**47.0**	**29291**
A17	He	8	65	NaI	25	47.0	7888
A18	He	1	90	NaI	23	121.1	192490
A19	**He**	**2.2**	**90**	**NaI**	**23**	**121.1**	**79182**
A20	He	8	90	NaI	23	121.1	20593
A21	Air	1	65	LiCl	11	20.7	28328
A22	Air	1	90	LiCl	10	52.6	75480
A23	He	1	65	LiCl	11	20.7	28328
A24	**He**	**2.2**	**65**	**LiCl**	**11**	**20.7**	**12680**
A25	He	8	65	LiCl	11	20.7	3455
A26	He	1	90	LiCl	10	52.6	75480
A27	He	2.2	90	LiCl	10	52.6	32952
A28	He	8	90	LiCl	10	52.6	8850
A29	Air	1	65	LiBr	5.3	9.9	13451
A30	Air	1	90	LiBr	5.3	27.9	38634
A31	He	1	65	LiBr	5.3	9.9	13451
A32	**He**	**2.2**	**65**	**LiBr**	**5.3**	**9.9**	**6070**
A33	He	8	65	LiBr	5.3	9.9	1662
A34	He	1	90	LiBr	5.3	27.9	38634
A35	He	2.2	90	LiBr	5.3	27.9	17198
A36	He	8	90	LiBr	5.3	27.9	4671

4.1.1 Key Test Details

Performing these tests required an oven capable of heating from 30°C–100°C ±2°C. The VWR model 1350FM oven was selected for this work. The pressure vessel selected 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. 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 needed 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 sensor selected is a Vaisala probe model HMP4. Swagelok 300 cm^3 U.S. Department of Transportation compliant 316 stainless steel sample bottles were selected for this test. 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, NaI, LiCl, and LiBr were used. The system was calibrated before testing was started.

One of the first steps for this test was to pre-treat sample bottles by heating them in the oven. The oven was set to 90°C and the samples were heated for 16–24 hours. During this time, the sample bottles were evacuated to less than 5 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 a refrigerator (nominally at 4°C) until use.

Next, the following process was repeated at the pressures, temperatures, gases, and liquid/salt solutions specified in Table 4. A measured amount of water and salt (if needed) was placed in the pressure vessel for the tests specifying those conditions as outlined in Table 5. A sample of the DIW was taken to measure isotope ratios using the Los Gatos Isotope Water Analyzer (see Section 4.2). Based on solubility data, this mixture will ensure that the solution will be fully saturated at up to 100℃. 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.

Table 5. Masses of water and salt used in the pressure vessel for Test A

Test Conditions	Mass DI H_2O (g)	Mass Salt (g)
Water only – vertical probe	826.0	n/a
Water only – horizontal probe	1001.0	n/a
NaCl – vertical probe	1001.6	395.4
NaCl – horizontal probe	993.0	383.5
NaI – vertical and horizontal configurations	1078.3	3213.7
LiCl – vertical probe, limited horizontal probe tests	1002.9	1311.1
LiBr – vertical probe only	1033.5	2697.5

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 at the desired pressure, and the oven was set to the desired temperature. The data acquisition system was started to record pressure, temperature, and hygrometer data. The cover gas was bled off as necessary to maintain the desired pressure during heating. The system was allowed to equilibrate for several hours to overnight. When the pressure, temperature, and hygrometer readings as % relative humidity (%RH) had stabilized, data was manually recorded. The Vaisala probe was initially tested in a vertical configuration directly in the pressure vessel headspace. After several tests, to ensure the best data possible, the probe was moved to the horizontal configuration directly above the pressure vessel as recommended by Vaisala as the optimal installation configuration. The horizontal configuration data had larger errors from the expected values, so the probe was returned to a vertical configuration for the remainder of testing. The thermocouple that monitored the temperature of the water/salt slurry broke mid-way through testing and was replaced with an uncalibrated thermocouple

to continue testing. The replacement thermocouple's performance was verified and calibrated at the end of testing. When gas samples were taken, pretreated sample bottles were connected. 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. This process was repeated a second and third time to take duplicate and triplicate samples. The oven temperature was then increased to the next set point and repeated without changing the cover gas. The Vaisala probe measurements are summarized in the next section.

The relative humidity measurement results summarized in the next section were plotted versus the expected relative humidity as calculated from the coefficients published by Greenspan (1977) (see Table 6) and the equation below:

$$RH = \sum_{i=0}^{3} A_i t^i = A_0 + A_1 t^1 + A_2 t^2 + A_3 t^3 \quad (2)$$

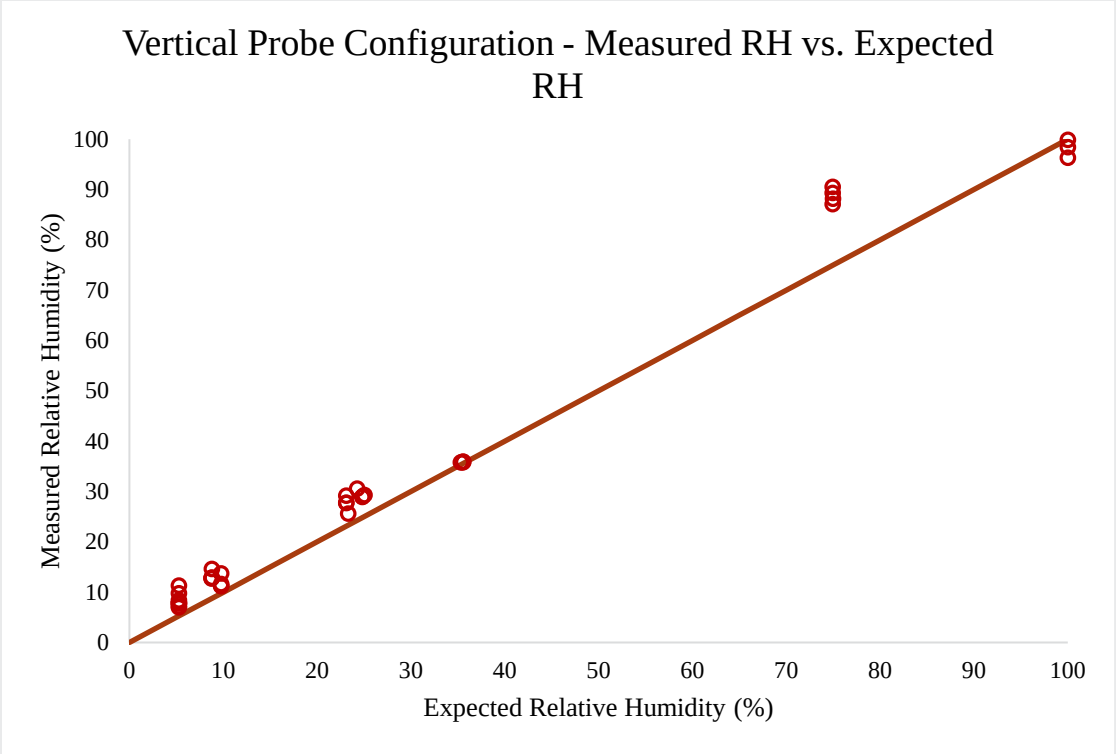
Where A_i is the salt-specific coefficient as published by Greenspan and t_i is the temperature (in °C) as measured by the Vaisala humidity probe.

Table 6. Relative humidity coefficients as published by Greenspan (1977)

Salt	A_0	A_1	A_2	A_3
NaCl	75.5164	0.0398321	-2.65e-3	0.00002848
NaI	42.604	0.00854045	-0.0093332	7.61055e-5
LiCl	11.2323	-0.00824	-0.00021	n/a
LiBr	7.775437	-0.0654994	0.000420737	n/a

4.1.2 Test A Results

The Vaisala probe relative humidity measurements in the vertical configuration in the headspace of the pressure vessel are plotted in Figure 5 vs. the expected relative humidities in addition to the measured ppmv humidity vs. expected ppmv. The ppmv water content values were calculated from the measured relative humidity and are subject to any errors associated with the pressure measurements as well as any errors related to the relative humidity readings. The relative humidity measurements of the probe in the horizontal configuration are plotted vs. the expected relative humidities in addition to the measured ppmv humidity vs. expected ppmv are shown in Figure 6. For the most part, across the range of relative humidities tested, the vertical configured probe had ratios to expected relative humidities closer to 1 than the horizontally-configured probe, which was not directly in the pressure vessel headspace but a horizontally configured fitting connected to the pressure vessel. This horizontal configuration likely did not provide adequate mixing between sampling points. Over most of the testing range, the measured values were biased high. The measured values are listed in the tables in Appendix A along with the ratios of the measured to calculated expected values. Further observations (not shown in this report) showed that the probe when positioned in the manifold did not provide an accurate reading of the humidity levels in the pressure vessel.



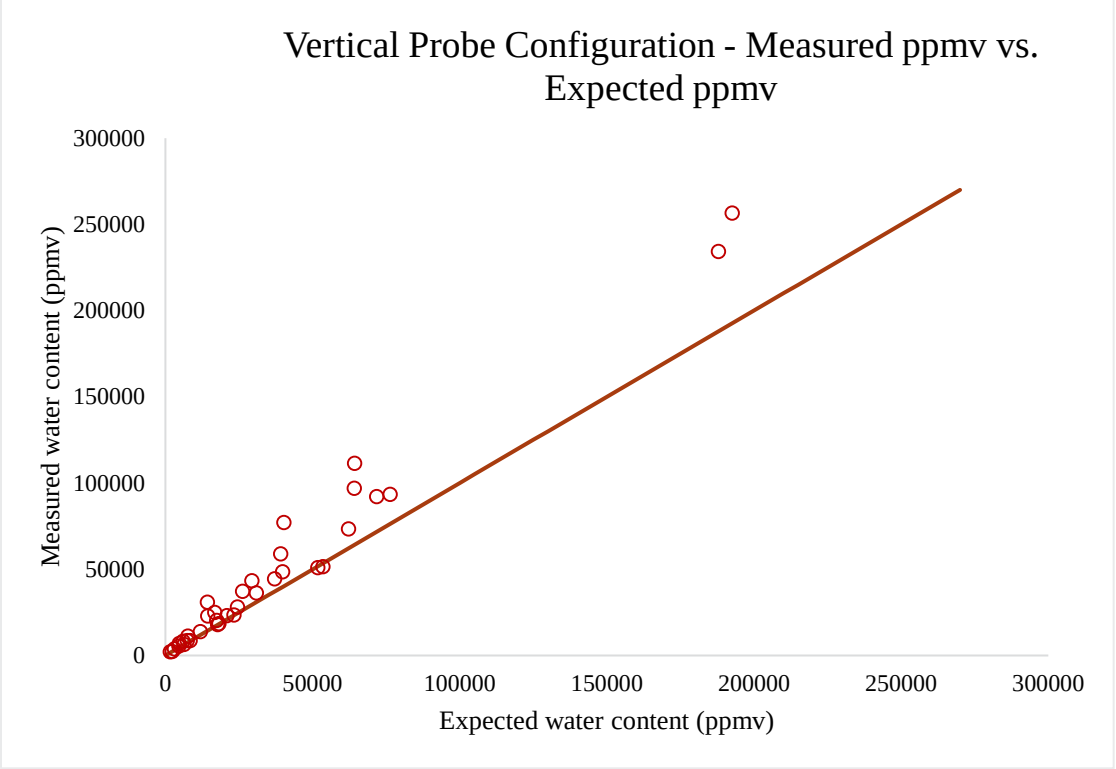
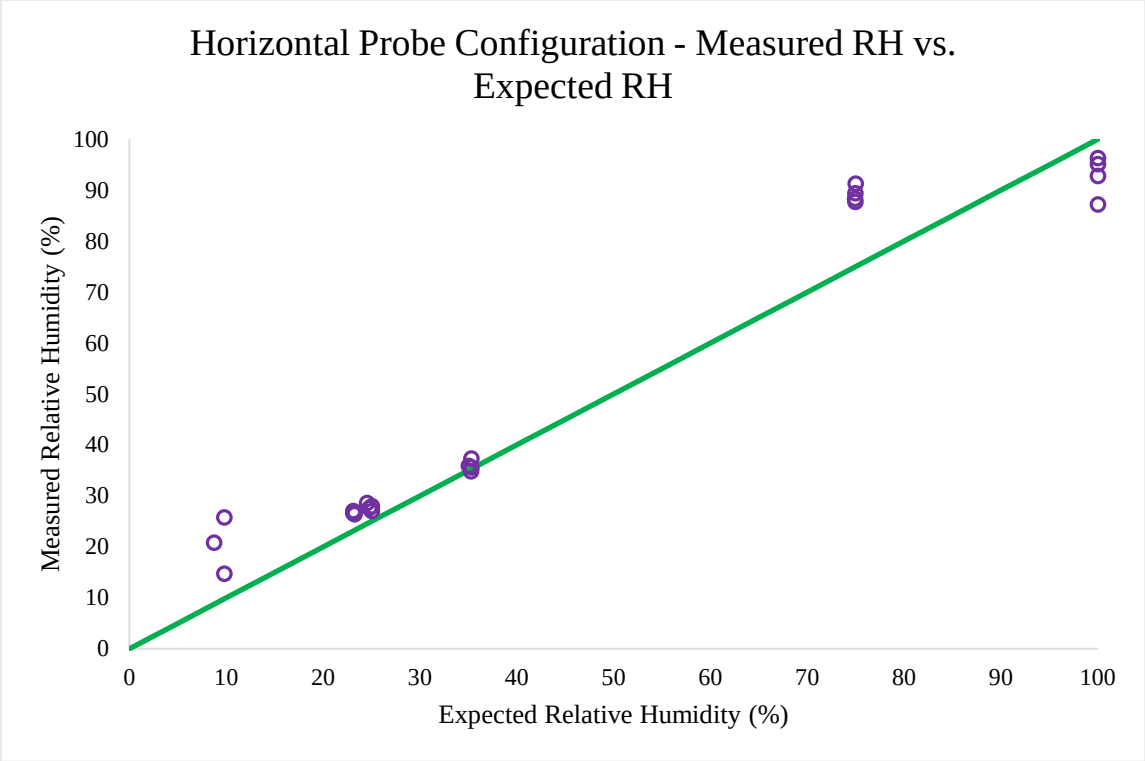


Figure 5. Measured vs. Expected calculated results for relative humidity (top) and Measured vs. Expected calculated results for water content (ppmv) as calculated from the relative humidity shown at bottom from the Vaisala humidity probe positioned vertically in the pressure vessel headspace.



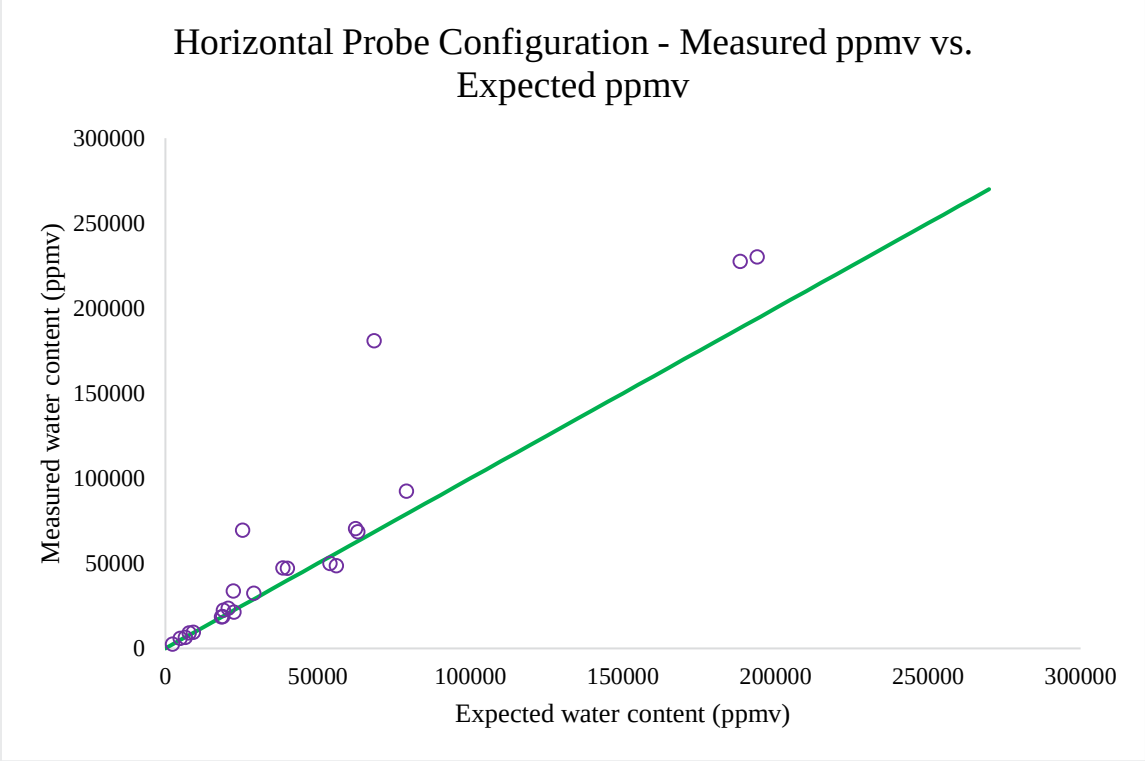


Figure 6. Measured vs. Expected calculated results for relative humidity (top) and Measured vs. Expected ppmv water content calculated from the relative humidity, temperature and pressure from the Vaisala humidity probe positioned horizontally above pressure vessel headspace.

4.2 Test B – Sample Bottle Measurements and Method Development

This test series is designed to increase confidence in the sampling measurement approach used by SNL for the sample 3 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. Additionally, the test also employs lessons-learned documented by Bryan et al. (2019b) for using an isotopic tracer and gravimetric measurements as alternative approaches for water vapor measurements from the gas samples. This test involves re-creating a similar test setup used to measure the water vapor for sample 3 at SNL. The setup—shown in the top photo of Figure 7—consists of placing the sample bottle in an oven along with the pressure gauges and humidity sensor. Using this setup, SNL was able to heat the sample bottles to 65°C. In this test, heating the sample bottle to 90°C has been used to date. A valved septum fitting (not shown) is used to inject D_2O tracer into the bottle prior to testing and sample collection, and a cold trap to collect condensed water (Figure 7 bottom photo). This setup allows for evaluation of three different water vapor measurement techniques:

1. Solid-state sensor measurements
2. Gravimetric measurements
3. Isotopic tracer measurements to determine the original moisture content.

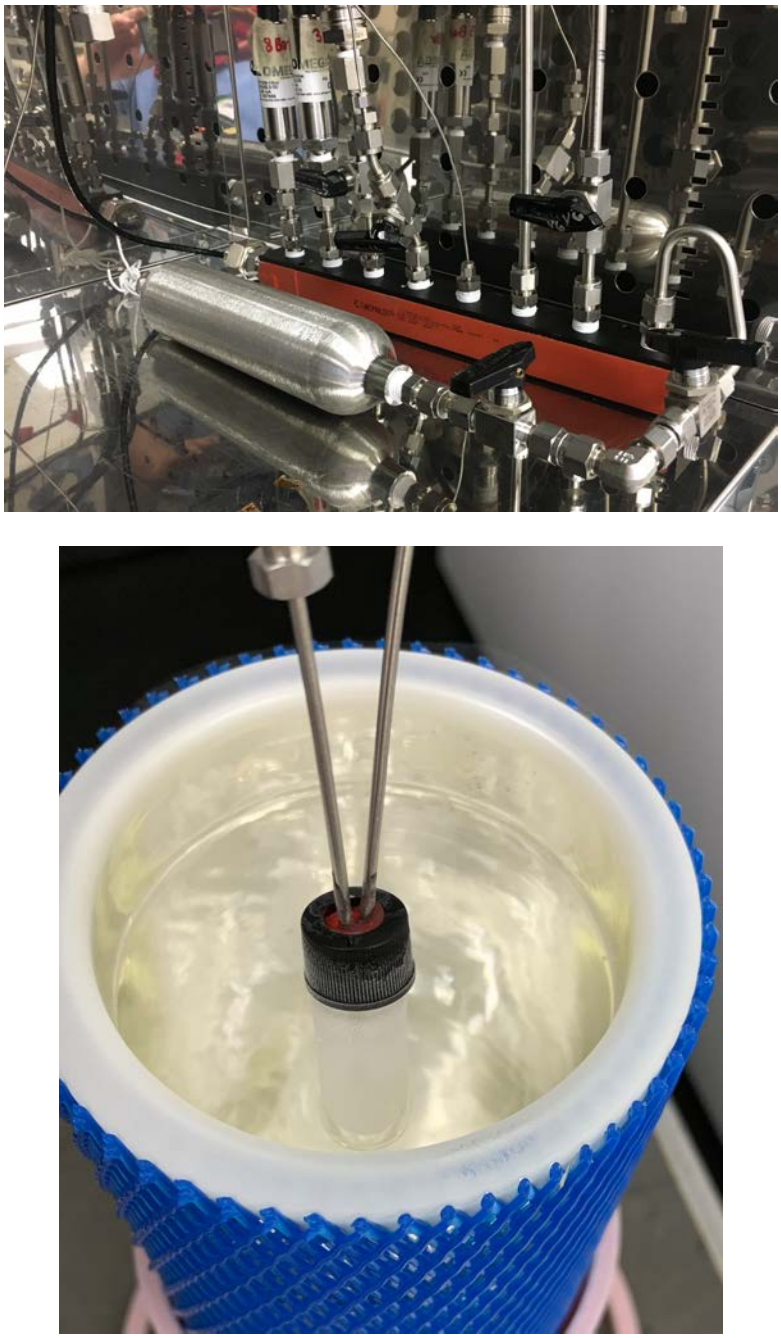


Figure 7. Sample Bottle Equipment for Test B. Top: Photograph of 300-cm^3 sample bottle connected to the manifold for bottle sampling. Bottom: Cold trap

Table 7. Test Matrix for Tests A and B Sampling

Test ID#	Gas	P (bar)	T (℃)	Source Liquid	Relative Humidity (%)	Vapor Pressure (Torr)	Water Concentration (ppm)
B1	He	2.2	30	DIW	100	31.8	19685
B2	He	2.2	30	NaCl	75	23.9	14691
B4	He	2.2	65	NaI	25	47.0	29291
B5	He	2.2	90	NaI	23	121.1	79182
B6	He	2.2	65	LiCl	11	20.7	12680
B8	He	2.2	65	LiBr	5.3	9.9	6070

In total, 18 sample bottles were collected under the conditions described in Table 7, 6 sets of 3 bottles. The bottles were stored at room temperature. After sample bottle collection, water-only tests were performed to determine the isotope ratio of the water in the vapor phase of each experiment to determine the optimal design for water trapping. Additionally, scoping studies were performed to evaluate isotopic mixing times and isotope exchange on bottle surfaces to help refine the method. During these scoping studies, it was determined that the current configuration will allow for an adequate amount of water to be trapped directly from the pressure vessel for isotopic analyses, however, water that was stored in sample bottles was not successfully trapped. As a result, one set of bottles was analyzed with the humidity probe installed in the manifold in the horizontal configuration, the details of which are summarized in section 4.2.2. The results show a much lower relative humidity in the bottles than expected, more method development is required.

Once a method for bottle sampling has been determined and the sample bottles are filled as specified above in Table 7, two approaches can be used to determine the amount of water in the sample bottle. The first approach is by directly measuring the mass of water retained in the cold trap system. The second approach relies on using a tracer material containing a known isotope ratio that has a different isotope ratio than the water used in testing. A known amount of deuterated water or ^{18}O enriched water is injected in the sample bottle as a tracer. A sufficient quantity of tracer will be used to provide a noticeable shift in isotope ratios while a known amount of deuterium depleted water will be added to the collected sample to provide adequate volume of approximately 100 µL for sample analysis. The isotopic ratio of the sample will be measured using a Los Gatos Research Liquid Water Isotope Analyzer Model DLT-100 (see Figure 8). Based on this process, Equation (3) can be used to determine the mass fraction of water in the sample bottle. Note that the Los Gatos Water Isotope analyzer will simultaneously measure the ratios of ^{2}H to ^{1}H as well as the ratio of ^{18}O to ^{16}O, and that the output of the DLT-100 is the ratio in form of an isotope ratio relative to the Vienna Standard Mean Ocean Water. These values are "delta" notation and are presented as $\delta^{2}H$ and $\delta^{18}O$. Because the equations use the difference of these values as a fraction, the reference values and conversion factors cancel out if the same reference value is used for all measurements. Therefore Equation (3) can be modified to use the oxygen isotope ratio, $\delta^{18}O$, as shown in Equation (4).

$$m_i = \frac{\delta^2 H_s - \delta^2 H_t}{\delta^2 H_i - \delta^2 H_s} m_t \quad (3)$$

$$m_i = \frac{\delta^{18} O_s - \delta^{18} O_t}{\delta^{18} O_i - \delta^{18} O_s} m_t \quad (4)$$

where m_i is the initial mass of $^{1}H_2{}^{16}O$ the sample bottle before tracer addition,

m_t is the mass of ^{1}H or ^{16}O calculated as $^{1}H_2{}^{16}O$ added to the sample bottle in the tracer mixture,

$\delta^2 H_s$ and $\delta^{18} O_s$ are the measured isotope ratios from the samples collected in the cold trap,

$\delta^2 H_i$ and $\delta^{18} O_i$ are the measured isotope ratios of the source water that is loaded into the

sample bottles,

$\delta^2 H_t$ and $\delta^{18} O_t$ are the measured isotope ratios of the tracer mixture injected into the sample bottle.

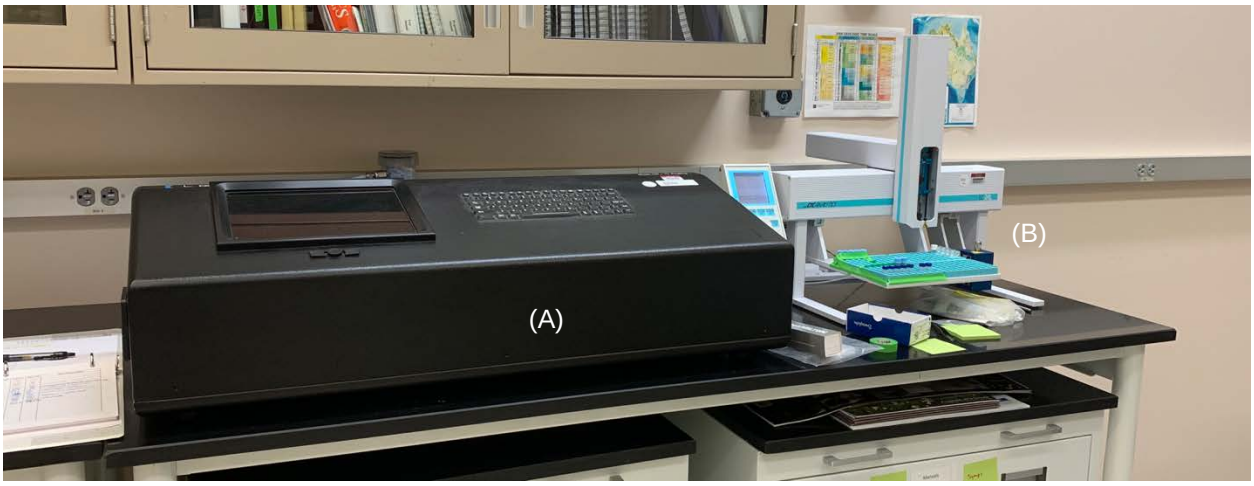


Figure 8. Photograph of Los Gatos Water Isotope Analyzer Model DLT-100 (A) with Autosampler (B) at the William R. Wiley Environmental Molecular Sciences Laboratory at PNNL.

4.2.1 Key Test Details

Once the correct sampling method has been determined, there will be 18 gas samples collected as shown in Table 7 (there will be triplicates of six samples). The samples will be stored at ambient temperatures for at least 1 week. A set of six sample bottles will be sent to SNL for humidity measurements. The other two sets of sample bottles will be measured for humidity at PNNL using the test setup shown in Figure 7. First, the tracer mixture tracer mixture isotope ratios will be measured with the Los Gatos Isotope Water Analyzer. This will provide the $\delta^2 H_t$ and $\delta^{18} O_t$ values for Equations (3) and (4). Sample bottles will be placed in the oven with connections to the hygrometer, pressure transducer and thermocouples. Next, the tracer mixture will be injected into the sample bottle by loading ~1-10 μL of tracer into syringe as directed by the cognizant scientist. The valve connecting the septa to the bottle will be opened and a syringe will be used to inject the tracer into the bottle. The mass of the tracer injected will be measured. This will provide the value for m_t for Equations (3) and (4). Next, the sample bottle will rest for several hours to 24 hours (as determined by the scoping studies) so the contents can reach isotopic equilibrium. The sample bottle will then be connected to the manifold system for analysis.

Next, the data acquisition system will be started to record pressure, temperature, and hygrometer information. The valve to the pressure, temperature, and, hygrometer sensors will be opened. The oven will be heated initially to 30℃. When the system has stabilized, stable pressure, temperature, and, hygrometer data measurements will be recorded. The temperature will be increased in +10℃ increments until 90℃ is reached with stable measurements being recorded at each temperature step.

Next, the water from the sample bottle will be collected in the cold trap. The mass of the empty trap will be recorded. The trap will be immersed in an ice/water bath to act as a condenser. The valve to the cold trap will be opened to bleed the sample bottle gas through the cold trap. The mass of the filled cold trap will be recorded. The contents of the trap will be collected in a sample vial with an insert for isotopic analysis. The sample vial contents will be measured with the Los Gatos Isotope Water Analyzer to obtain isotope ratios, which will provide the $\delta^2 H_s$ and $\delta^{18} O_s$ values for Equations (3) and (4). The DIW sample used to produce the sample bottles will be measured with the Los Gatos Isotope Water Analyzer to obtain

isotope ratios. This will provide the $\delta^2 H_i$ and $\delta^{18} O_i$ values for Equations (3) and (4). Finally, the water quantity in sample bottle, m_i, will be calculated using Equations (3) and (4).

4.2.2 Test B Results to Date

During the water-only testing and the start of the initial scoping studies, it was observed that little to no discernable water was trapped from the scoping sample bottles that were filled from a water-only filled pressure vessel (i.e. at 100% RH). To verify that the water trap collection was not the problem, one set of the sample bottles were analyzed as described above by connecting the bottle to the manifold with the Vaisala probe in place, starting at 30°C, the temperature was increased by 10°C each hour and manual measurements collected until the temperature reached 90°C and stabilized. The measured relative humidities from the bottles were very low compared to the measurements collected in the pressure vessel headspace during bottle-filling in Test A when accounting for the expansion volume to the manifold. Bottle B2 had a particularly low 'as found' pressure reading indicating that the bottle may have had a leak. The results of this set of analyses are summarized in Tables 8 and 9 below. It is important to determine how to fill a bottle with a representative relative humidity, as the current method does not appear to collect a representative sample. Moving forward we will explore other possible geometries for sampling including larger sample bottles, mounting the sample bottle directly to the pressure vessel to minimize condensation points due to expansion and finally testing the isotopic and/or gravimetric trapping method directly from the pressure vessel.

Table 8. Sample Bottle Filling Conditions from Test A

Test A	Temp (C)	Expected RH (%)	Measured RH (%)	Water Content (ppmv)	System Pressure (bar)	Expected vapor pressure (Torr)	Expected vapor pressure (bar)	Test B
A3	30	100	100.3	18896	2.29	38.9	0.052	B1
A7	30	75	87.1	16685	2.254	38.5	0.051	B2
A16	65	24.8	28.9	37546	2	180.5	0.24	B4
A19	90	23.1	27.8	96354	2.216	509.5	0.68	B5
A24	65	9.8	11.3	13620	2.106	188.8	0.25	B6
A32	65	5.3	7.2	8245	2.205	187.1	0.25	B8

Table 9. Preliminary sample bottle measurement results, measured relative humidity and pressure at 30°C, 60°C and 90°C and expected pressure at 30°C.

Test B ID	Water Content (ppmv) 30C	Measured Pressure (bar) 30C	Expected expansion pressure 30C (bar)	Water Content (ppmv) 60C	Measured Pressure (bar) 60C	Water Content (ppmv) 90C	Measured Pressure (bar) 90C
B1	753	1.862	1.96	4884	2.011	15983	2.186
B2	152	0.836	1.93	887	0.900	5768	0.979
B4	112	1.517	1.54	858	1.629	4092	1.722
B5	266	1.435	1.58	3483	1.609	20954	1.744
B6	105	1.615	1.62	689	1.739	3725	1.891
B8	77	1.664	1.69	557	1.791	3256	1.946

4.3 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.

The samples will be autoclaved to form an oxide layer and placed in a water bath to saturate the surface. The samples then will be placed in a drying oven and held at stepwise increasing temperatures. Sample mass will be 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. At the time of the writing of this draft report, the autoclave is still undergoing modifications to be operational and in compliance with PNNL's pressure safety requirements.

4.3.1 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 Table 1. Six samples for each of four cladding tube types will be tested. Prior to autoclaving each cladding, samples will be measured for length, diameter, thickness, and mass.

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

samples will then be placed in a water bath at 60°C for 1 week. At the end of the week, the samples will be air-dried at ambient temperature and then measured 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 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.

4.4 Test D – Small-Scale Drying of Cladding

For this test series, the contribution of humidity to the backfill gas from water desorbed from the surface of cladding material will be studied before and after vacuum drying at a temperature consistent with measurements made on the HBDP cask during vacuum drying. For this test, the cladding array will initially be oxidized and saturated with water. Four different conditions were 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. (2019a). 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 10. Due to schedule limitations, only Test ID# D4 was planned for each cladding type in FY2020, however, these tests are not yet completed due to issues with the autoclave startup.

Table 10. 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

Last, the vessel will be backfilled with helium to 2.2 bar, and humidity will be monitored to determine a steady-state water vapor concentration. 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. (2020).

Bryan et al. (2019a) 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 (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 3 will be used for this test. Instead of a salt solution, an array of cladding materials will be used in the arrangement shown in Figure 9. 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 surface area ratio is 0.67 cm. For a full-scale cask, the ratio is ~0.66 cm.

Figure 9. Photograph of Actual Cladding Tube Holders for Test D. The holder for PWR clad tubes is on the left (A) and BWR clad tubes is on the right (B).

4.4.1 Key Test Details

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 Table 1. 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 system components described in Section 4.1.1 will be used for the testing. 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 80–90°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 10. 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 Figure 1. In addition, the final humidity level in the system will be compared to the actual cask measurements.

4.5 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 a mockup guide-tube/dashpot will be studied before and after vacuum drying at a temperature consistent with measurements made on the HBDP cask during vacuum drying. The mockup of a guide-tube/dashpot will be initially filled with a test solution. Four different conditions will be tested. Two conditions correspond to the guide-tube/dashpot mockup being filled with DIW prior to testing and the other condition will fill the guide-tube/dashpot 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 guide-tube/dashpot mockup will lead to increases in humidity as postulated by Bryan et al. (2019a) 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 11. Due to schedule limitations, only Test ID# E4 was planned in FY2020, however, this test is not yet completed.

Table 11. 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

Finally, the vessel will then be backfilled with helium to 2.2 bar, and humidity will be monitored to determine a steady-state water vapor concentration. 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. (2020).

The system shown in Figure 3 will be used for the small-scale test of the guide-tube/dashpot system. Instead of a salt solution, a guide-tube/dashpot system will be used in an arrangement similar to that

shown in Figure 10–left, which is provided by Yoon et al. (2009). This diagram that was used as the basis for the mockup system on Figure 10–right.

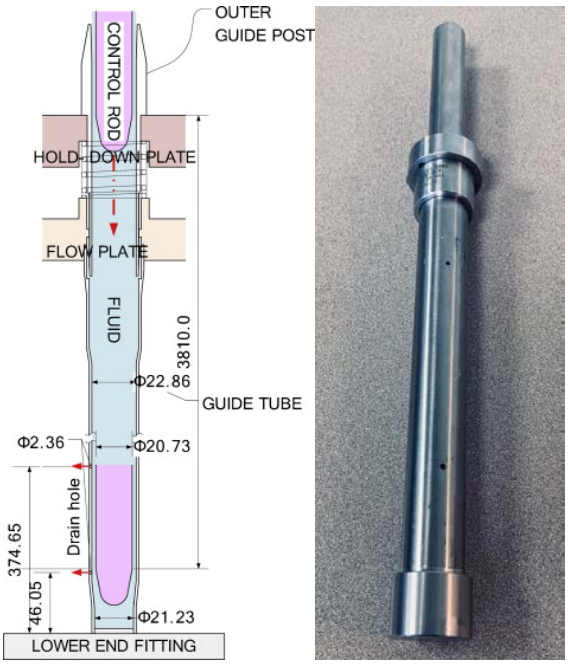


Figure 10. Schematic Drawing of a Guide-Tube/Dashpot and Control Rod Assembly Model from Yoon et al. (2009) (left) and Mockup System (right).

The mockup consists of a single 22.23-mm inner-diameter tube, a 20-mm outer-diameter inner rod, and 2.36-mm (0.087") diameter drain holes. The mockup is designed to have a similar free volume below the bottom drain hole of about 12.3 mL and an annular gap distance of ~2.2 mm. Because of the size of the mockup, a larger 3 gallon pressure vessel will be used for this test. The tube will be loaded with a known amount of DIW and a solution of 2500 ppm boron (14,300 ppm H_3BO_3) as potential water vapor sources. The system will be tested with simulated vacuum drying prior to the applying the rebound test acceptance criteria of that the pressure remain below 4 mbar (3 Torr) after 30 minutes. At the conclusion of the test, any free water remaining in the tube will be measured.

4.5.1 Key Test Details

With the exception of the pressure vessel, the system components described in Section 4.1.1 will be used for the testing. To accommodate the height of the guide-tube/dashpot mockup, a larger pressure vessel is required. The pressure vessel selected is manufactured by Alloy Products Corporation out of 316L stainless steel with a 3 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 guide-tube/dashpot mockup. This will be accomplished by loading the guide-tube/dashpot mockup into the pressure vessel and placing the vessel in the oven. Next, the oven will be set at 80–90°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).

After the vessel cools, the guide-tube/dashpot mockup will be filled to the lower drain hole with a solution consistent with Table 11. 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 11. 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 from system 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 to <1% difference over 24 hours. After cooling, the guide-tube/dashpot mockup will be inspected visually and gravimetrically, if possible, for the presence of any free liquid. If free liquid is found, its mass will be measured.

Subsequent tests will be initiated by cleaning the guide-tube/dashpot mockup and placing the mockup back into the pressure vessel for pre-conditioning. Transient humidity levels for all test conditions will be plotted to see if any match the linear profile in Figure 1. In addition, the final humidity level in the system will be compared to the actual cask measurements.

5. SUMMARY

This report documents the experimental background, design, key procedure steps, and interim testing status of the small-scale drying tests slated to be performed 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 taken at the North Anna Nuclear Generating Station for the HBDP. Specifically, the purpose of these tests is to support SNL gas sample methods and analyses through a series of five small-scale experiments that include:

- *Test A, Method Development and Sample Bottle Loading* – The purpose is to increase confidence in the sampling and measurement sensor technology used for the SNL sample 3 humidity results.
- *Test B, Sample Bottle Measurements* – The purpose is to increase confidence in the sampling measurement approach used by SNL for the sample 3 humidity results through an PNNL/SNL inter-laboratory comparison of results from gas samples taken from controlled conditions using saturated salt solutions to achieve target humidity levels. Additionally, the test also will employ lessons-learned documented by Bryan et al. (2019b) for using an isotopic tracer and gravimetric measurements as alternative approaches for water vapor measurements from the gas samples.
- *Test C, Surface Drying Tests* – The purpose is to measure the amount of water desorbed from the surface of 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 the contribution of humidity to the backfill gas from water desorbed 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 the contribution of humidity to the backfill gas 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.

Results to date from Test A show that the Vaisala humidity probe relative humidity measurements are close to the expected relative humidity values when in direct contact with the vessel headspace. When the probe was placed in a horizontal configuration above the pressure vessel headspace, the results were more variable. The 300 mL sample bottles that were filled in Test A were found to have dramatically lower water content values from those found in the pressure vessel headspace when they were filled, requiring more investigation and method development to be performed to understand if the sample bottles provide a representative sample of cask conditions. The bottle filling configuration will be adjusted to minimize tubing lengths which may be the cause of the discrepancy in the current data set. The remainder of the testing is underway and will be presented in a subsequent report.

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6. REFERENCES

Bryan, C. R., Durbin, S. G., Lingren, E., Ilgen, A. G., Montoya, T. J., Dewers, T., & Fascitelli, D. (2019a). *SNL Contribution: Consequence Analysis for Moisture Remaining in Dry Storage Canisters After Drying (SAND2019-8532 R).* Albuquerque, NM: Sandia National Laboratories.

Bryan, C. R., Jarek, R. L., Flores, C., & Leonard, E. (2019b). *Analysis of Gas Samples Taken from the High Burnup Demonstration Cask (SAND2019-2281).* Albuquerque, New Mexico: Sandia National Laboratories.

Electric Power Research Institute (EPRI). (February 27, 2014). *High Burnup Dry Storage Cask Research and Development Project: Final Test Plan (Contract No.: DE-NE-0000593).* Palo Alto, CA: Electric Power Research Institute (EPRI).

Electric Power Research Institute. (2019). *High Burnup Dry Storage Research Project Cask Loading and Initial Results (3002015076).* Palo Alto, CA: Electric Power Research Institute.

Greenspan, L. (1977). Humidity Fixed Points of Binary Saturated Aqueous Solutions. *Journal of Research of the National Bureau of Standards—A. Physics and Chemistry, 81A*(1), 89-96.

Hanson, B. (October 24, 2018). High Burnup Spent Fuel Data Project & Thermal Modeling and Analysis. *NWTRB Meeting.* Albuquerque, NM.

Jung, H., Shukla, P., Ahn, T., Tipton, L., Das, K. H., & Basu, D. (2013). *Extended Storage and Transporation: Evaluation of Drying Adequacy (Contract NRC-02-07-006).* San Antonio, TX: Center for Nuclear Waste Regulatory Analyses.

Kochsiek, M. (1982). Measurement of Water Adsorption Layers on Metal Surfaces. *Metrologia, 18*(3), 153-159.

Lin, L. (2014). *Controlling CRUD Vapor Chimney Formation in LWRs Through Surface Modification.* Cambridge: Massachusetts Institute of Technology.

Salazar, A., Pulido, R. J., Lindgren, E. R., & Durbin, S. G. (2020). *Development of Mockups and Instrumentation for Spent Fuel Drying Tests (SAND2020-5341 R).* Albuquerque, NM: Sandia National Laboratories.

Spinks, J. W. (1990). *An Introduction to Radiation Chemistry, 3rd Ed.* New York: John-Wiley and Sons, Inc.

Yoon, K. H., Kim, J. Y., Lee, H. K., Lee, Y. H., & Kim, H. K. (2009). Control rod drop analysis by finite element method using fluid–structure interaction for a pressurized water reactor power plant. *Nuclear Engineering and Design, 239*(10), 1857-1861.

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Appendix A

Test A Measurements

Table A1. Test A vertical probe relative humidity measurements

Test #	Gas	Salt	Oven Temp (°C)	Headspace Temp (°C)	Liquid Temp (°C)	Pressure (bar)	Measured Relative Humidity (%)	Vaisala Probe Temp (°C)	Calculated Relative Humidity (%)	Ratio of Measured RH (%) to Expected RH (%)
A1	Air	--	31.7	31.5	30.9	1.002	96.3	33.1	100.0	0.96
A2	He	--	31.6	31.3	30.8	1.000	98.4	32.6	100.0	0.98
A3	**He**	**--**	31.8	32.0	32.0	2.288	100.3	33.6	100.0	1.00
A4	He	--	31.5	31.0	31.8	8.007	99.9	32.9	100.0	1.00
A5	Air	NaCl	31.6	31.6	31.7	0.995	90.5	33.1	75.0	1.21
A6	He	NaCl	31.7	31.6	31.5	1.063	89.3	33.1	75.0	1.19
A7	**He**	**NaCl**	31.7	31.9	31.7	2.251	87.1	33.4	74.9	1.16
A8	He	NaCl	31.3	31.5	31.8	8.131	88.2	32.8	75.0	1.18
A9	Air	NaI	31.1	31.3	31.5	0.995	35.9	32.8	35.5	1.01
A10	Air	NaI	67.9	65.1	63.3	0.981	30.6	66.6	24.3	1.26
A11	Air	NaI	91.0	88.1	87.9	0.974	29.2	89.1	23.1	1.26
A12	He	NaI	31.9	31.7	31.6	1.007	35.9	32.6	35.6	1.01
A13	He	NaI	32.2	31.9	31.7	2.120	35.8	32.8	35.5	1.01
A14	He	NaI	32.6	32.5	32.1	8.073	35.8	33.4	35.3	1.01
A15	He	NaI	63.8	62.0	61.8	0.994	29.3	63.3	25.1	1.17
A16	**He**	**NaI**	64.9	62.9	62.2	1.998	28.9	64.2	24.8	1.16
A17	He	NaI	64.7	62.9	62.2	8.148	29.0	64.1	24.8	1.17
A18	He	NaI	90.7	88.3	88.1	0.993	27.7	89.2	23.1	1.20
A19	**He**	**NaI**	90.7	88.4	88.2	2.216	27.8	89.2	23.1	1.20
A20	He	NaI	91.6	89.5	88.9	8.107	25.6	90.4	23.3	1.10

Test #	Gas	Salt	Oven Temp (°C)	Headspace Temp (°C)	Liquid Temp (°C)	Pressure (bar)	Measured Relative Humidity (%)	Vaisala Probe Temp (°C)	Calculated Relative Humidity (%)	Ratio of Measured RH (%) to Expected RH (%)
A21	Air	LiCl	64.2	64.1	63.9	0.977	13.7	65.3	9.8	1.40
A22	Air	LiCl	88.8	88.1	87.7	0.984	14.6	88.9	8.8	1.66
A23	He	LiCl	64.7	63.7	62.9	1.022	11.2	64.9	9.8	1.14
A24	**He**	**LiCl**	64.9	64.1	63.5	2.105	11.3	65.2	9.8	1.16
A25	He	LiCl	65.0	64.3	63.9	8.086	11.6	65.3	9.8	1.19
A26	He	LiCl	88.9	88.9	87.6	0.986	12.9	89.0	8.8	1.47
A27	He	LiCl	89.7	89.2	88.5	2.151	12.8	89.8	8.8	1.46
A28	He	LiCl	89.5	89.1	88.5	8.040	12.7	89.8	8.8	1.45
A29	Air	LiBr	64.5	64.4	64.1	0.977	11.3	65.6	5.3	2.14
A30	Air	LiBr	89.5	89.2	89.0	0.968	9.8	90.1	5.3	1.86
A31	He	LiBr	63.8	64.8	65.4	0.964	8.4	65.6	5.3	1.59
A32	**He**	**LiBr**	63.8	63.3	63.0	2.205	7.2	65.0	5.3	1.37
A33	He	LiBr	63.7	63.3	63.1	8.047	7.0	64.4	5.3	1.33
A34	He	LiBr	89.5	89.1	88.8	0.982	7.8	89.9	5.3	1.48
A35	He	LiBr	89.9	89.1	88.8	2.260	7.8	90.0	5.3	1.48
A36	He	LiBr	89.7	89.0	88.8	8.018	7.8	89.9	5.3	1.48

Table A2. Test A horizontal probe relative humidity measurements

Test #	Gas	Salt	Oven Temp (°C)	Headspace Temp (°C)	Liquid Temp (°C)	Pressure (bar)	Measured Relative Humidity (%)	Vaisala Probe Temp (°C)	Calculated Relative Humidity (%)	Ratio of Measured RH (%) to Expected RH (%)
A1	**Air**	--	**32.9**	**32.9**	**32.6**	**0.996**	87.2	33.8	100.0	0.87
A2	He	--	32.8	32.8	32.6	1.017	92.8	33.6	100.0	0.93
A3	He	--	32.7	33.0	326	2.373	95.1	33.6	100.0	0.95
A4	He	--	33.0	32.7	32.3	8.061	96.3	33.8	100.0	0.96
A5	Air	NaCl	31.8	31.7	31.6	1.000	91.3	32.6	75.0	1.22
A6	He	NaCl	32.4	32.2	31.7	1.000	87.7	33.3	75.0	1.17
A7	He	NaCl	33.0	32.8	32.3	2.129	88.3	33.9	74.9	1.18
A8	He	NaCl	32.6	32.7	32.7	8.071	89.4	33.5	74.9	1.19
A9	Air	NaI	32.8	32.5	32.4	0.993	34.8	33.5	35.3	0.99
A10	Air	NaI	63.5	62.0	61.8	0.988	27.0	63.4	25.0	1.08
A11	Air	NaI	90.5	88.0	87.9	0.968	26.6	89.1	23.1	1.15
A12	He	NaI	32.6	32.4	32.4	1.009	35.6	33.4	35.3	1.01
A13	He	NaI	33.4	33.1	32.9	2.074	35.9	34.1	35.1	1.02
A14	He	NaI	32.7	32.6	32.6	7.903	37.3	33.4	35.3	1.06
A15	He	NaI	63.6	62.0	61.5	0.993	28.0	63.4	25.0	1.12
A16	He	NaI	64.6	62.9	62.4	2.147	27.6	64.4	24.8	1.11
A17	He	NaI	65.6	63.8	63.3	8.066	28.6	65.3	24.6	1.16
A18	He	NaI	90.6	88.1	87.9	0.988	27.0	89.1	23.1	1.17
A19	He	NaI	91.6	88.8	88.5	2.216	26.8	89.9	23.2	1.15
A20	He	NaI	91.6	89.0	88.9	8.031	26.4	89.9	23.2	1.14
A21	Air	LiCl	63.7	63.5	63.4	0.979	25.8	64.5	9.8	2.63
A22	Air	LiCl	90.1	89.3	89.0	0.964	20.8	90.2	8.7	2.38
A23	He	LiCl	63.7	63.4	63.0	1.104	14.7	64.5	9.8	1.50