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Analysis of Gas Samples Taken from the High Burnup Demonstration Cask

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ABSTRACT

The High Burn-Up Demonstration Project was recently initiated by the Department of Energy (DOE) to evaluate the effects of fuel drying and long term dry storage on high burn-up spent nuclear fuel. As part of the project, samples of the He backfill gas were collected 5 hours, 5 days, and 12 days after completion of drying. The samples provide information on the state of the fuel at closure, and on the environment within the cask. At Sandia National Laboratories, the samples were analyzed by gamma-ray spectroscopy to quantify fission product gases and by gas mass spectrometry to quantify bulk and trace gases; water content was measured via humidity probe. Gamma-ray spectroscopy results indicated no detectible ^{85}Kr, indicating no failed fuel rods were present after drying. Mass spectrometry indicated build-up of CO_2 to 930 ppmv over two weeks, attributed to oxidation of organic compounds (possibly vacuum grease or vacuum pump oil) within the cask. H_2, generated by either radiolysis or metal corrosion, also increased up to ~500 ppmv. Water contents in the cask were higher than anticipated, increasing to ~17,400 ppmv ±10% after 12 days. Measuring water content proved challenging, and possible improvements to the method for future analyses are proposed.

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EXECUTIVE SUMMARY

For long-term storage, spent nuclear fuel (SNF) is placed in dry storage systems, where it may remain for decades prior to eventual disposal in a permanent repository. To evaluate the effects of fuel drying and long term dry storage on high burn-up fuel, the Department of Energy (DOE) and industry collaborators have initiated the High Burn-up Demonstration Project. High burn-up fuel was transferred to a dry storage cask and the cask was dried using standard industry vacuum-drying techniques. It was then placed on a storage pad for ageing, to be opened and the fuel examined in 10 years. The project has several different goals, but one of them was to evaluate the composition of the cask helium backfill, and to track its evolution over time. Of particular interest is the amount of water in the cask gas phase, and whether any liquid water could present in a cask after drying. Water content in the cask is important because it may eventually react with metals in the cask, corroding cask internals or cladding. The analysis also evaluated fission gases, providing information on the possible presence of damaged or leaking rods in the cask after completion of the drying process.

One-liter gas samples were taken from the demonstration cask at three intervals: 5 hours, 5 days, and 12 days after the backfilling and sealing. Samples were analyzed for water content at ambient temperatures at the North Anna Power Station, and additional samples were shipped to Sandia National Laboratories for more complete analysis. Samples were initially counted using gamma-ray spectroscopy (400,000 second count) to determine if fission gases were present. the analysis focused on ^{85}Kr, for which gamma spectroscopy is highly sensitive. No ^{85}Kr was observed in any of the samples. Gas aliquots were then analyzed for water content, and by direct gas mass spectrometry to determine non-sorbing (i.e., permanent) gases. The mass spectrometric analysis provided concentrations of non-sorbing gases in the samples. Several important trends were observed, including increases in carbon dioxide (CO_2) up to 930 ppmv and hydrogen (H_2) up to nearly 500 ppmv after 12 days of storage. Trace amounts of organic compounds were also observed. We hypothesize that the CO_2 was generated by reactions between a hydrocarbon contaminant (likely vacuum grease used on the pump fittings, and/or vacuum pump oil) and oxidizing species produced by water radiolysis. Increasing H_2 concentrations may also be due to radiolysis, followed by consumption of the accompanying oxidizing species by oxidation of the organic material or by metal corrosion. However, if anoxic conditions exist in the cask, H_2 may also be produced by direct reduction of water by metals in the cask.

To measure water content, a Vaisala humidity probe was attached to each bottle, and the sample was heated in steps to desorb water adsorbed to the bottle interior. Heating proved to be critical for accurate water quantification—the water content measured at ambient temperature was only $^2/_3$ of the total water measured at 65ºC. Final results indicated that the cask gas water content increased to a value of 17,400 ppmv ±10% after 12 days—equivalent to approximately 100 ml of water within the entire cask gas phase. The measured water value corresponds to les than 10% relative humidity at the minimum expected temperature in the cask at the time of sampling (~85ºC). If the cask gas phase is compositionally homogeneous, then liquid water is not present within the cask, unless trapped in inaccessible locations.

ACRONYMS AND DEFINITIONS

Abbreviation	Definition
DOE	Department of Energy
ppmv	parts per million (volume)
psia	pounds per square inch (absolute)
psig	pounds per square inch (gauge)
SEM	secondary electron multiplier
SNF	spent nuclear fuel
SNL	Sandia National Laboratories

1. INTRODUCTION

In November of 2017, the cask for the High Burnup Demonstration Project was filled with fuel from the spent fuel pool at the North Anna Power Station. The demonstration project is primarily intended to evaluate the effects of dry storage on high-burnup fuel, but a secondary goal is to evaluate the gas composition within the cask and how it changes over time. To do this, samples of the cask fill gas were collected 5 hours, 5 days, and 12 days after closure. The primary goal of the gas sampling was to verify the efficiency of the drying process used for the dry storage cask. The samples also provided l information regarding the state of the spent fuel; the presence of fission gases, especially ^{85}Kr, would indicate breached cladding.

At North Anna, a vacuum drying method is used, in which the water is siphoned from the cask and then a vacuum is pulled on the canister while the fuel heats to above-boiling temperatures. The vacuum used for drying is relatively low, about 0.55 mbar (0.41 Torr). Once drying is thought to be complete, sufficient dryness is demonstrated by sealing the canister and measuring the pressure rise over time. Any pressure rise would be due gas generation—presumably water evaporation or desorption—within the cask. The requirement is that the pressure remain below 4 mbar (3 Torr) after 30 minutes. Following drying, the canister was backfilled with He and sealed. Gas samples were collected 5 hours, 5 days, and 12 days after closure. Two sets of the gas samples were collected at each sampling interval. The first was analyzed by Dominion Energy at the North Anna site, using a Water Vapor Isotope Analyzer from Los Gatos Research. The second set was sent to Sandia National Laboratories (SNL) for analysis using several different techniques as described below.

1.1. Sample bottle pre-treatment

The sample bottles used for testing were assembled by Dominion Energy; an example is shown in Figure 1. Each sample bottle consisted of a Swagelok one liter stainless steel bottle with ¼" tubing on both ends with a septum for gas sampling and a pressure gauge attached to one end. Both ends of the sampling rig were sealed with a ¼ turn plug. Because the SNL samples would be subjected to several analyses, requiring longer storage times, the three sample bottles for SNL were modified. High-quality needle valves were attached directly to each end of the sample bottle and the septum riser was removed. The pressure gauge and ¼ turn ball valve on the other end of the sample bottle were retained but were placed outside the needle valve.

Prior to collecting the samples, both sets of bottles were pre-treated at SNL to minimize the amount of water sorbed to the inside of the bottles. The bottles were wrapped in heating tape and heated to 80-90ºC for 16-24 hours, while being pumped under a mid-to-high vacuum of nominally 1.3×10^{-10} bar (10^{-7} Torr), estimated at 1.3×10^{-9} bar (10^{-6} Torr) within the bottle. Note that although ¼ turn valves on the Dominion bottles were worked during pumping to remove as much air as possible, valves would still outgas or leak upon motion, increasing the vacuum pressure to around 1.3×10^{-8} bar (10^{-5} Torr) for the Dominion bottles. After heating and pumping, the canisters were filled with a gauge pressure of 1.38 bar (~20 psig) ultra-high purity He and returned to the North Anna Power Station for sample collection.

Figure 1. Sample Bottles, as Designed by Dominion Energy.

1.2. Samples

Samples were collected from the Demo Cask at three intervals as shown below:

- 11/16/17 15:21 (~5 hours after helium backfill)
- 11/21/17 11:47 (5 days after helium backfill)
- 11/28/17 08:34 (12 days after helium backfill)

During sampling, gas pressures in cask were recorded as approximately 2.2 bar (absolute). Samples were shipped to SNL and received within a few days of sampling. Gauge pressures upon delivery of the samples to SNL were recorded to be about 1.38 bar (20 psig), which is consistent with recorded pressure in the cask:

1.38 bar + 0.86 bar (Albuquerque atmospheric pressure) = 2.24 bar

1.3. Methods

Upon receipt at Sandia, each sample was immediately analyzed by gamma-ray spectroscopy (Section 2) to determine if the samples were radioactive—which could have placed restrictions on the other proposed analytical methods. Following gamma counting, the samples were transferred to a second laboratory for analysis by direct gas mass spectrometry to determine other gaseous compounds in the He fill gas, with a detection limit in the few ppm range (Section 3). This method is applicable for analysis of non-sorbing gases (O_2, N_2, H_2, CH_4), but offers only qualitative estimates of the amount of water present. To quantify water, additional analyses were carried out. This proved to be more difficult than anticipated, and three different methods were eventually attempted, as described Section 4. The final method involved attaching the sample bottle to a tee assembly with a humidity meter and a pressure gauge, heating the samples in a oven to drive water desorption from the sample bottle interior wall, and measuring the water content as a function of temperature.

2. GAMMA-RAY SPECTROSCOPY

The gamma-ray spectroscopy was performed with a Canberra closed-end coaxial high purity germanium detector. Sample bottle geometry was modeled using Genie/ISOCS™ software as a simple cylinder of 304 SS, with overall dimensions and wall thicknesses corresponding to those of the Swagelok® sample bottles. Each sample was counted within its steel bottle, first for 12 hours, and then a second time, for ~4.6 days (400,000 seconds). The long count yielded high sensitivity, but resulted in a complex background spectrum—even muon interactions with the lead shielding were detected.

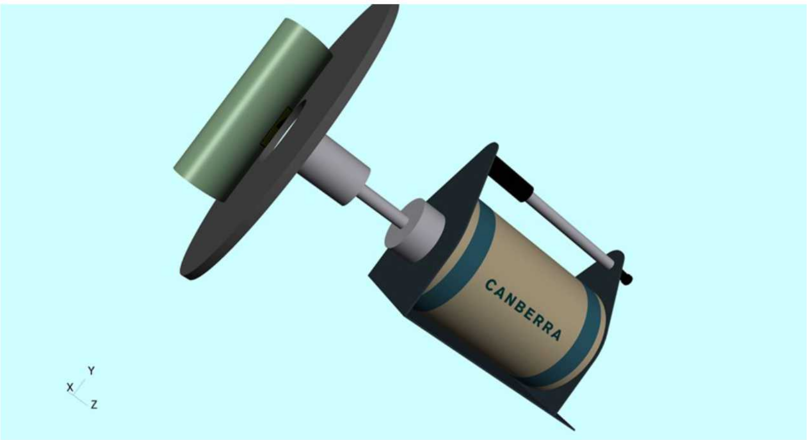

Figure 2. Assumed sample geometry for gamma-ray spectroscopy.

Gamma-ray spectroscopy is highly sensitive for ^{85}Kr because of its high specific activity (~400 Ci/g) and high energy gamma rays (514 keV). However, gamma counting would not detect a second radioactive fission gas, ^{129}I, because of its low specific activity (1.7×10^{-4} Ci/g) and its weak gamma (40 keV), which would not penetrate the walls of the sample bottle.

For all three samples, there was no detectible ^{85}Kr peak (514 keV) in either the short or long count. However, it should be noted that the 4.6-day count was sufficiently long that the background electron-positron annihilation peak at 511 keV became significant, potentially interfering with detection of extremely low levels of ^{85}Kr. The 511 keV peak is visible in Figure 3, which shows the overlaid spectra for Samples 1 and 3. The presence of the 511 keV peak (12,024 counts, consisting of a peak of 8,140 counts on a background of 3,884 counts) and the relatively low production rate for the ^{85}Kr 514 keV gamma ray (0.43% of all decays) affects the detection of ^{85}Kr. The approximate detection limit was estimated using the methods of Currie (1968) to be about 38 Bq, or 2.57×10^{-12} g within the sample bottle.

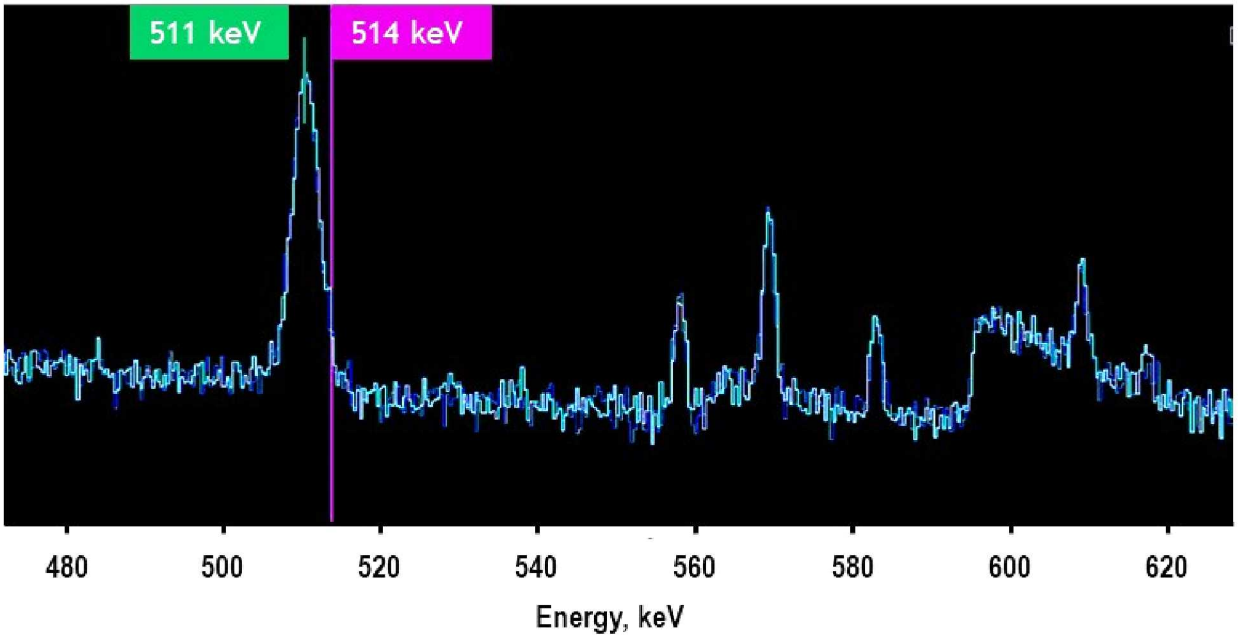

Figure 3. Overlaid gamma-ray spectra for Samples 1 (dark blue) and 3 (light blue), for a 400,000 second count. The visible peaks, including the positron-electron annihilation peak at 511 keV, are part of the background. There is no observed peak at 514 keV, the primary ^{85}Kr gamma ray.

3. MASS SPECTROMETRY

Once gamma-ray spectroscopy was completed, the samples underwent compositional analysis by mass spectrometry to determine bulk composition and the abundances of trace-level gases.

3.1. Analysis Method

The gas analyses were performed using a Finnigan MAT 271 high-resolution mass spectrometer. This instrument is a magnetic sector mass spectrometer, specifically tailored for hydrogen isotope measurements and utilizing a very stable gas ionization source. The mass spectrometer was operated with resolution of approx. 1200 and 1600 ($m/\Delta m$), using Faraday cup detector #4 and a secondary electron multiplier (SEM) detector, respectively. Detection sensitivity calibration for most of the identified permanent gas species was obtained using a verified precision gas mixture provided by Matheson Gas.

The three gas samples were delivered in one-liter cylinders, each pressurized to a gauge pressure of ~1.48 bar (20 psig). Each was attached to a high-vacuum system along with 50 cm^3 sample cylinders. The 50 cm^3 sample cylinders and the tubing to the valve on the sample bottles were evacuated overnight to very dry levels. The vacuum system was isolated and the sample bottle valve opened to allow gas into the 50 cm^3 cylinder. The 50 cm^3 cylinder was then removed, attached to the mass spectrometer inlet, and also evacuated up to its valve overnight before analysis. The original one-liter sample bottles, still containing most of the sample, were retained for later quantitative water measurements.

Gas measurement of the 50 cm^3 sample cylinders was performed using OP-ASGAS-008, a high-purity sampling and measurement procedure developed by SNL. The quantitative bulk-gas measurements were made using the Faraday cup detector, which is a low-noise ion collector; trace species were measured using the amplified SEM, which has a higher level of noise. Calibration gas response was verified on both detector channels during the same day as sample measurement.

3.2. Results

The relative molar quantities of the major gases detected for each of the samples are presented in Table 3-1. The N_2 values in this table are accurate to about ± 2% relative (2σ level), or 0.005% absolute, whichever is greater. Values for water are qualitative and considered order-of-magnitude indicators, as there are many adsorption-desorption effects for sorbing gases that occur during sample introduction and transfers within the stainless-steel inlet system. In general, the water content is underestimated when it is present in trace amounts, and overestimated at higher concentrations. The measured concentrations are high, and hence, should be overestimates. This is confirmed by the fact that the values for Samples 2 and 3 are not actually possible—they exceed the saturated water content of gas at 2.2 bars and ambient temperatures (See Section 4).

Table 3-2 lists the trace gas species which were detected at quantifiable levels. Uncertainty in this table is estimated at ±8% relative to the amount indicated. The N_2 signal for Sample 1 was outside the detector's range and caused a large shoulder which precluded measurement of the CO concentration in this sample.

The gas composition within the cask appears to be evolving on the time scale of weeks, based upon the changes observed in Table 3-2. There were relatively large amounts of water in every sample, more in Samples 2 and 3 than in Sample 1. High nitrogen concentrations probably indicate sample contamination with air, particularly in Sample 1 but to a lesser degree in Samples 2 and 3. The amount in Samples 2 and 3 may be consistent with that expected to be introduced by the sampling methodology (e.g., air trapped in the valves or in the quick-release fitting on the cask).

Table 3-1. Bulk Gas Compositions of Demo Cask Samples

Gas Species	Sample 1	Sample 2	Sample 3
Sampling date	11/16/2017 15:21	11/21/2017 11:47	11/28/2017 8:34
He	Confirmed balance gas		
H_2O (est.)	0.46%	1.8%	2%
N_2	0.39%	0.07%	0.07%

Table 3-2. Concentrations of Trace Level Gases.

Gas Species	Sample 1 (ppmv)	Sample 2 (ppmv)	Sample 3 (ppmv)
H_2	46	287	498
CH_4	< 1	9	22
CO	nm	34	25
N_2	off scale	630	680
O_2	680	38	134
Ar	49	8	9
CO_2	103	751	930

nm – not measurable due to large N_2 signal interference.

Carbon dioxide levels likewise rise markedly in the last two samples, to 930 ppmv in Sample 3. This is a significant mass of carbon—if representative of the cask gas, it corresponds to approximately 3.5 grams carbon within the cask gas phase. The source of the carbon is uncertain, but it was likely present as organic material that reacted with oxygen and oxidizing radicals generated by radiolysis to produce the CO_2. The general reaction for oxidation of hydrocarbons produces water and CO_2 via:

$$C_xH_y + (x + y/4)\ O_2 \rightarrow xCO_2 + y/4\ H_2O$$

One possible source of organic material would be vacuum pump oil. The North Anna facility uses an EMS Solutions Inc. E1000 Vacuum Drying System, which is a dry vacuum pump. However, the gear box for the system is connected to the vacuum pump via a port to eliminate any pressure differentials, and the gear box is lubricated with Krytox 1514, a low vapor pressure synthetic perfluoropolyether. Back-streaming of small amounts of oil through the pump and into the cask is a possible source for organic contamination and the observed CO_2 levels. A small peak consistent with hydrogen fluoride (HF) was present in Sample 3 at the 10 ppm level. This could be caused by the degradation of a Krytox or a similar fluorocarbon oil compound within the cask. However, vacuum pump oils are designed to have a low vapor pressure; perhaps a more likely source is vacuum grease, which according to Dominion Energy personnel was liberally applied to the pump fittings prior to attaching the vacuum line to the cask. In addition of HF, Sample 3 has other unique features not shown in Table 3-2 that support the presence of organic material in the cask. There are unquantified yet clear indications of low-level (low-ppm) concentrations of ethane/ethene and either formaldehyde or alcohol. Since the HF and short-chain organics were present in only the last of the 3 samples, it appears that the internal cask environment is slowly evolving.

Hydrogen levels increased in the successive samples, reaching about 500 ppmv by the 3rd sample. There are two possible sources for the hydrogen. The first is direct metal reduction of H_2O to produce H_2, a reaction which occurs under anoxic conditions (if this is the case, the observed oxygen concentrations would have to be from air contamination during sampling). The second possible source of H_2 is radiolysis of water, which also produces oxygen/reactive oxidizing radicals that could react with metal. This can be considered radiolysis-mediated corrosion. However, there is an additional sink for the oxidizing species produced by radiolysis—the organic material that was oxidized to form the elevated levels of CO_2 in the cask gas. Hence, the buildup of H_2 does not necessarily indicate that a commensurate level of metal corrosion has occurred.

4. WATER ANALYSIS

One of the primary goals of the high burnup demonstration cask gas sampling program was to determine the water content of the fill gas, and how that changed over time. Gas samples were collected and analyzed for water at North Anna by Dominion Energy. These samples were analyzed with the sample bottles at room temperature, and it was recognized that the measured values do not account for the effects of water sorption onto the interior of the sample canisters. The samples were sent to SNL for more thorough analysis that included heating the samples to desorb water from the sample bottle interior, allowing a more accurate quantification of the sample water content.

It was recognized from the beginning that water sorption to the metal sample canister must be accounted for. This required that the sample bottles be thoroughly dried prior to use, as described in Section I.A, and then during analysis, heating the samples to desorb water from the bottle walls. Had the sample bottles not been thoroughly dried initially, then water desorbing from the sample bottle into a dry gas sample would have resulted in measured water values that were higher than the true values. Conversely, heating to desorb water from the sample bottle interior during analysis is critical to avoid underestimating the actual water content.

The water contents measured on-site by Dominion Energy for Samples 2 and 3 raised an additional concern. Initial estimates were in the range of 10,000 ppmv H_2O, which, at the sample pressure of about 2.2 bars, is close to saturation at room temperature (Figure 4). Given the uncertainties in the measurements, which had not been well quantified at the time, it was possible that water had condensed in the sample canisters. If so, then accurate measurement of the water content would require heating the canisters to evaporate that water back into the gas phase.

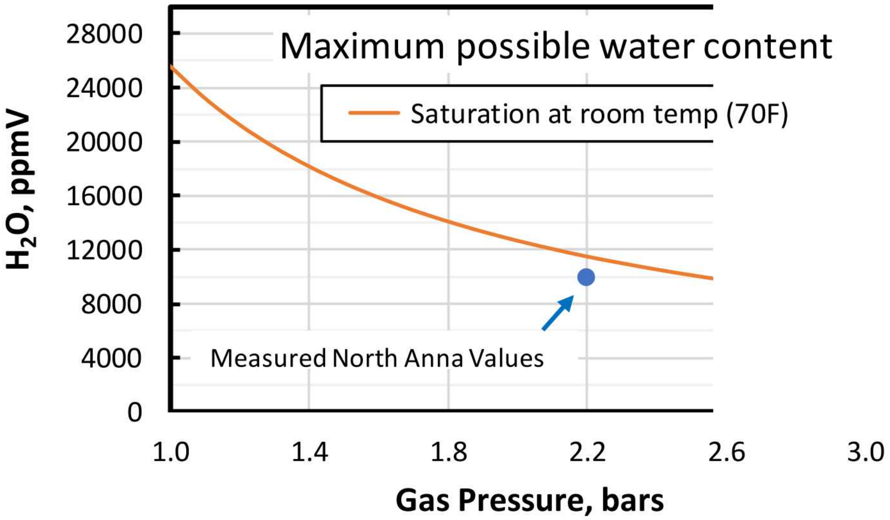

Figure 4. Sample Values Measured at North Anna were Close to Saturation at the Sample Pressures, Raising the Possibility of Condensation within the Sample Bottles.

4.1. Measuring Sample Water Contents

Several methods were tested to quantify the water contents of the gas samples were tested. The first method involved using an Agilent gas chromatograph model 6890 with a VICI model D4 pulsed discharge ionization detector were utilized. The method uses a helium flush of all the exposed plumbing and He blanks were analyzed between standards and samples to verify that no carryover was occurring. All samples were tested with a split ratio of 100:1 and same injection volume. Water contents were quantified by comparison to a calibration curve made using Frostpoint standards with known water content. However, the results of this method were highly erratic, varying from run to run, and in some cases exceeded the saturated water content at the sample pressure. It was not possible to heat the gas chromatograph inlet lines, and it is likely that water sorption/desorption effects as described in Section 3 for the gas measurements by magnetic sector mass spectrometer prevented accurate water measurements.

Subsequent efforts were carried out at the SNL Primary Standards Lab, which has extensive facilities for measuring gas-phase water contents and for calibrating probes to perform those measurements. Three different experimental setups were used, the first two failing to work as intended. The different designs are shown in Figure 5.

In the first attempt, the sample bottle was placed in a loop with a RH Systems dewpoint mirror, model 973, which contains an internal pressure gauge and pump. The bottle was placed in an oven for heating, and the ¼” stainless steel flexible tubing used for the loop was wrapped in heating tape between the oven and the chilled mirror. During heating, the tubing was maintained at a temperature 3ºC above the oven temperature to minimize water sorption. Prior to analysis, the tubing was purged with dry nitrogen overnight to remove any initial adsorbed water. Then, the purge was stopped, but dry nitrogen was left in the tubing at ambient pressure (~12.2 psi at Albuquerque altitude). This would have to be corrected for later to calculate water content. The valves on the bottle were then opened, and the internal pump circulated the gas through the loop and through the chilled mirror, allowing analysis of the water content. However, this design proved untenable—the pump within the chilled mirror developed a leak.

Following the failure of the first system, a different chilled mirror instrument (RH Systems Dewpoint Mirror, model 373) was used. This instrument did not contain an internal pump, so a small external diaphragm pump was placed in the loop. The entire system was pressure tested to about 2 bars, and as before, purged overnight with dry nitrogen. However, once a sample was attached, the external diaphragm pump heated up and failed within seconds of starting. At this point, it was clear that the high-quality needle valves on the sample bottle restricted gas flow too much, damaging the diaphragm pump and probably the pump within the original chilled mirror instrument as well. The continuous loop approach, required for a chilled mirror, could not be used for the samples.

In the final design, a tee was placed on one end of the sample bottle, with a pressure gauge attached to one arm and a Vaisala relative humidity (RH) probe (Model HMP77B, RH 0% to 100%, T −70ºC to 180ºC) attached to the other. The Vaisala probe could measure the sample water content statically. However, because of the restricted aperture of the needle valves, equilibration of the entire system at any given temperature took several hours. One advantage of this design was that the entire setup could be placed in the oven, eliminating the need for heating tape, and the possibility of uneven heating. The system worked well, with no leakage; pressures stabilized immediately and remained stable for days. Water content and pressure were measured at ambient temperature and at approximately 5ºC intervals up to 65ºC (pressure gauge temperature specifications prevented use of higher temperatures). Each sample was taken through the temperature ramp twice.

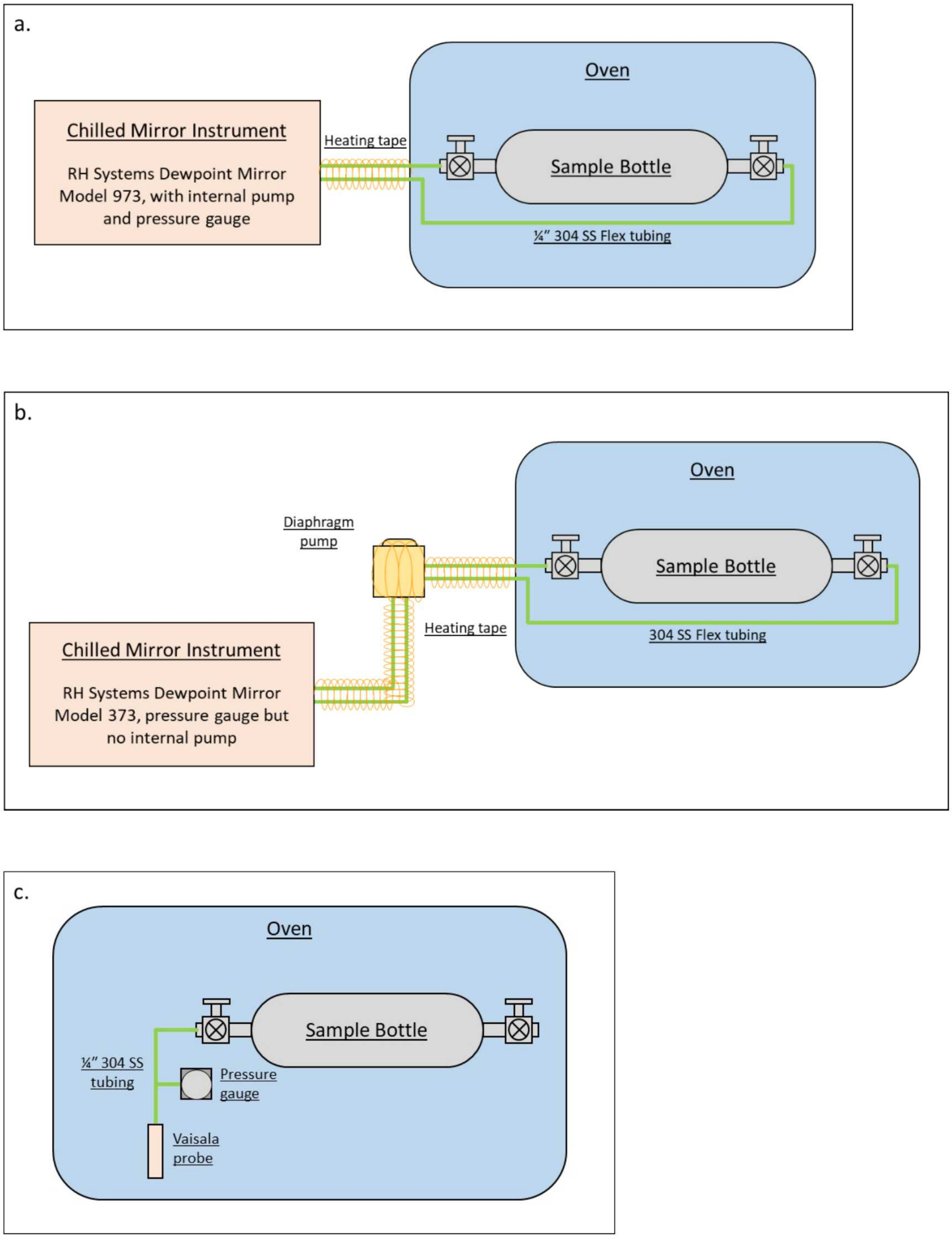

Figure 5. Three different experimental designs were tested for measuring sample water contents. a) sample attached to a loop with a chilled mirror with internal pump; b) sample attached to a loop with chilled mirror, and diaphragm pump; 3) sample attached to a dead-end tube with a Vaisala probe. Only the third design proved successful.

4.1.1. Sample #1

This sample was analyzed using the first system design (Figure 5a). To test the system, a 1 liter gas standard prepared by Thunder Scientific Corporation was analyzed first. The standard was nominally 11541 ppmv water in nitrogen at a pressure of 810.4 Torr and a temperature of 24.58ºC. Upon analysis, the standard measured 10,510 ppmv H_2O at 23.2ºC. Correcting for dilution by the dry nitrogen in the tubing, the measured water content of the standard was 10,980 ppmv. This value was within 5% of the standard value and was deemed acceptable.

Following the analysis of the standard, the system was once again purged with dry nitrogen overnight, and Sample #1 was placed in the loop. However, when the needle values were opened and the pump in the chilled mirror instrument started, the pump immediately developed a leak. The pressure, initially about 27 psi, rapidly dropped to about 13.7 psi, less than 2 psi above ambient. An accurate measurement of the water content was not possible, because the water content increased as gas was lost via the leak, as water desorbed from the canister walls in response to the decreasing vapor pressure. However, an initial reading, taken at a pressure of about 18.10 psi, was 2048 ppmv; correcting for dilution by the nitrogen in the loop tubing, and the 50 ml gas removed for mass spectrometer analysis, this is equal to a sample value of 2097 ppmv. This is a maximum value for a reading at ambient temperature (~25ºC), because the water content increased as gas was lost through the leak and the pressure dropped. Nonetheless, it is relatively consistent with the water content of ~1633 ppmv measured at ambient temperatures by Dominion Energy at the North Anna site (EPRI 2019). However, it may be an underestimate of the total water content, because water that remained adsorbed to the inside of the metal sample bottle and in the loop was not accounted for.

4.1.2. Sample #2

The first attempt to analyze Sample #2 used the second design (Figure 5b). As noted previously, the pump in this design failed immediately after opening the needle valves on the sample bottle. A measurement could not be taken, and the sample was compromised. Not only was the gas phase that was in the loop lost—there was no way to get it back into the bottle—but additional water that adsorbed out onto the walls of the loop was also lost.

Using the final design (Figure 5c), Sample #2 was taken through a temperature ramp twice. Measured data at each temperature step were corrected for the water lost as vapor in the loop in the previous attempt and for the 50 cm^3 sample used for mass spectrometer analysis; in both cases the water content measured at ambient temperatures was assumed to represent the gas that was lost. Adsorbed water lost in the loop could not be accounted for. Results for Sample #2 are summarized in Figure 6. Measured water contents for the two replicates vary significantly (Figure 6a), with the values for the second temperature ramp being consistently higher than the first. It is believed that this is because insufficient time was allowed for gas-phase equilibration throughout the test system in the first test. By the time of the second test, both water vapor and adsorbed water had become distributed evenly throughout the system, and equilibration was much faster. At ambient temperatures, the measured water content was about 6600 ppmv. This is significantly lower than the water concentrations measured on the sister sample at ambient temperatures at North Anna (8,896 ppmv; EPRI 2019), and is interpreted to indicate that considerable water was lost by sorption onto the inside walls of the loop tubing during the previous attempt (Figure 5b) to measure the water content of this sample. Hence, the measured values for this sample, under-represent what would have been present had the sample not been compromised. The water content increased with temperature as water desorbed from the inner walls of the sample bottle, illustrating the need to heat the samples during analysis. The water content appeared to level out between 60ºC and 65ºC, at a value of about 10,000 ppmv; once again, this should be taken as a minimum value. The RH was about 40% at ambient temperature, but decreased to about 8% at 65ºC (Figure 6b). The RH is equal to the water vapor pressure divided by the saturated vapor pressure at the same temperature (P_w/P_{sat}), and the drop in RH indicates that, although P_w increases with temperature as water desorbs from the bottle walls, P_{sat} increases much faster. Even allowing for the loss of water during the previous measurement attempt, it is clear that there was never any condensed water in the sample bottle. Finally, as expected for a fixed-volume system, system pressure increased linearly with temperature (Figure 6c).

4.1.3. Sample #3

Sample #3 was measured using the same experimental setup as Sample #2. Measured data are shown in Figure 7. The data have been corrected for the tiny change in water content due to the removal of the 50 cm^3 mass spectrometry sample. At ambient temperature (23ºC), the measured water content was about 11,200 ppmv, corresponding to an RH of about 78% (Figure 7a and Figure 7b). This value somewhat higher than the measured values at the North Anna site (8,300 ppmv; EPRI 2019). The water content increased with temperature, but appeared to level out between 50º and 65ºC, to a value of about 17,400 ppmv; corresponding to an RH of about 15%. Although the measured water contents at ambient temperature are relatively close to saturation, the drop in RH with increasing temperature indicates that no condensed water was present in the sample bottle. While some water probably remained adsorbed to the metal at 65ºC, it is unlikely to be significant, as the low RH would drive desorption of most of the water.

The sample pressure increased linearly with temperature, actually exceeding the cask pressure at temperatures over 55ºC (Figure 7c). This suggests that the gas cooled rapidly during sample collection, such that the pressure equilibrated between the sample bottle and the cask, but the average gas temperature in the sample bottle was lower.

4.1.4. Assessing uncertainty in measurements

To evaluate the analytical uncertainty in the measurements for the final experimental design (Figure 5c), a standard was measured using the same setup. The standard, purchased from Thunder Scientific Corporation, contained 6999 ppmv H_2O in nitrogen at 25.5ºC, with a total pressure of 2.2 bars. The standard was made by flowing humid nitrogen with the desired water content through the standard bottle for 24 hours prior to sealing the bottle, allowing complete equilibration between the adsorbed water in the bottle and water in the gas phase. The standard was analyzed twice, at approximately 25.7ºC, and measured H_2O contents were 6633 ppmv and 6686 ppmv (Figure 8). These values are about 5% low, but were deemed acceptable, given other uncertainties in the method. After the second analysis, the temperature was increased to see how much water would desorb from the metal sample bottle. The water content of the gas increased markedly as the temperature rose, with the concentration at 60ºC more than double the concentration at 25ºC. Unlike the samples from the high burnup demonstration cask, the water content in the standard increased nearly linearly with temperature, and showed no sign of leveling out at higher temperatures. We attribute this to the different model and inside finish of the standard bottle, which was furnished by Thunder Scientific.

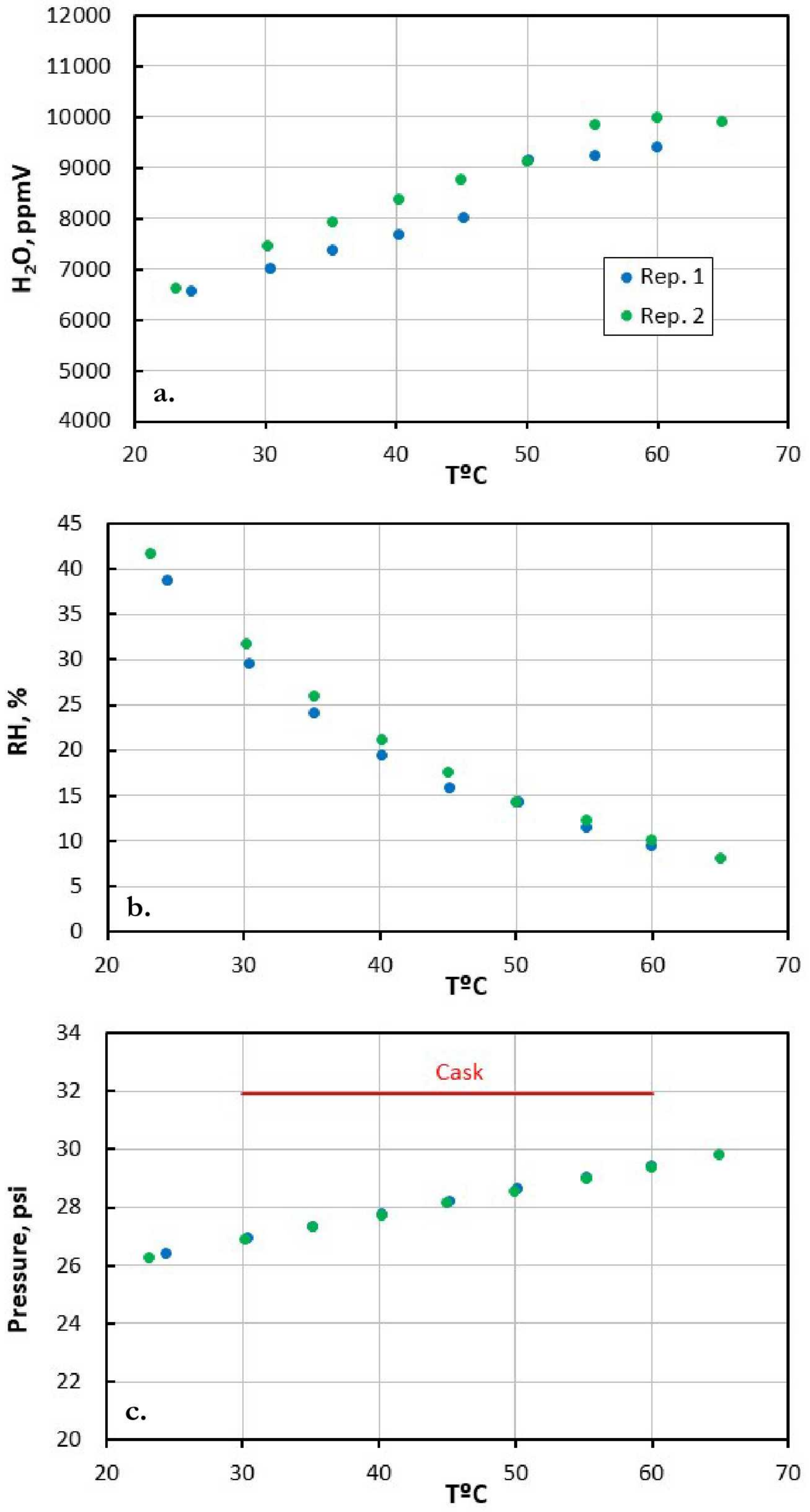

Figure 6. Measured results for Sample #2 as a function of temperature. a) H_2O content; b) RH; and c) pressure.

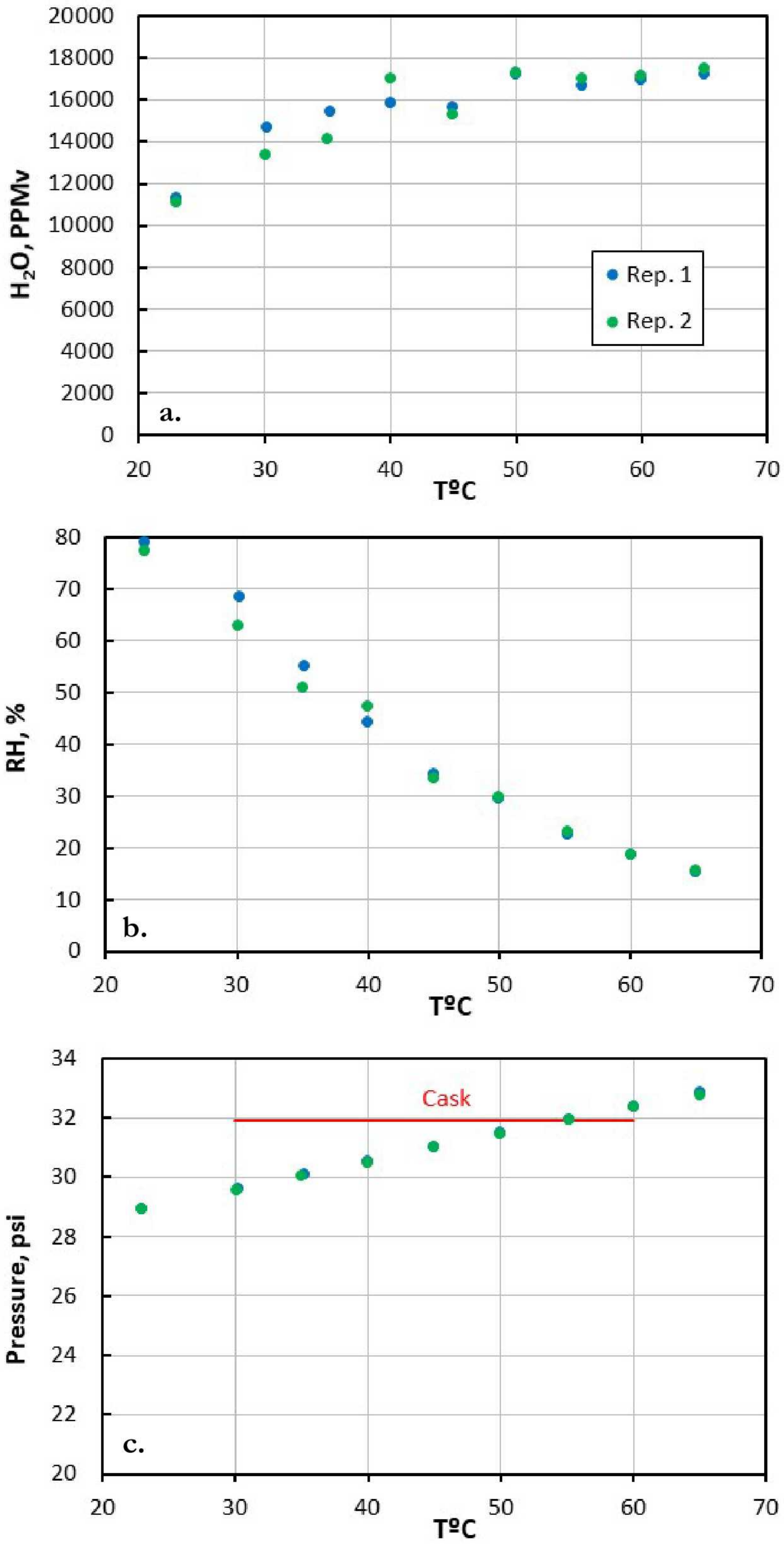

Figure 7. Measured results for Sample #3 as a function of temperature. a) H_2O content; b) RH; and c) pressure.

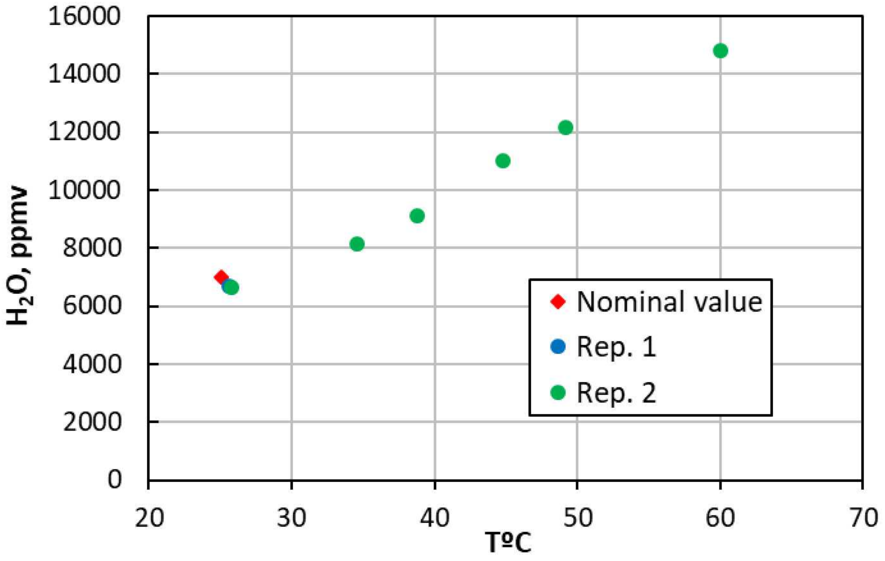

Figure 8. Measured results for gas standard (7000 ppmv H_2O at 25ºC, 2.2 bars nitrogen).

Two additional tests were carried out evaluate the accuracy of the Vaisala probe water measurements (Figure 9). In these tests, a humidity generator controlled by a RH Systems chilled mirror was used to generate a gas phase of known water content. The environments produced were checked using a second RH Systems chilled mirror instrument to verify their accuracy; values for the two instruments matched to within 1%. In the first test, the temperature was held constant at 21.1ºC, and the RH and water content were varied (Figure 9a). The measurement error for water content varied strongly with RH. Below 10% RH, the Vaisala readings were about 10% high. the error decreased as Rh increased, and was less than 4% above 25% RH. In the second test, RH was held constant at 11.1%, while the temperature was raised from ambient to 45ºC (Figure 9b). In this case, the Vaisala measurement error was constant at about 10%. Note that this value is consistent with the predicted value of at 10% RH in (Figure 9a). These data suggest that the Vaisala probe measurement uncertainty is controlled by the RH, regardless of temperature.

Note that all the errors shown in Figure 9 are positive; that is, the Vaisala probe consistently overestimated water content. Utilizing the data from Figure 9, the estimated error for Sample 3, measured at 65ºC and a RH of about 15%, would be about 7%. The measured value of 17,400 ppmv would have to be decreased by 7% to about 16,200 ppmv H_2O. *However*, these results are inconsistent with the value measured for the Thunder Scientific 2.2 bar, 7,000 ppmv H_2O standard, which were about 5% low. Given the discrepancy between the method uncertainty and uncertainty associated with the actual measurement device, it recommended not to adjust the values measured using the Vaisala probe, but instead to assume a measurement uncertainty of ±10%.

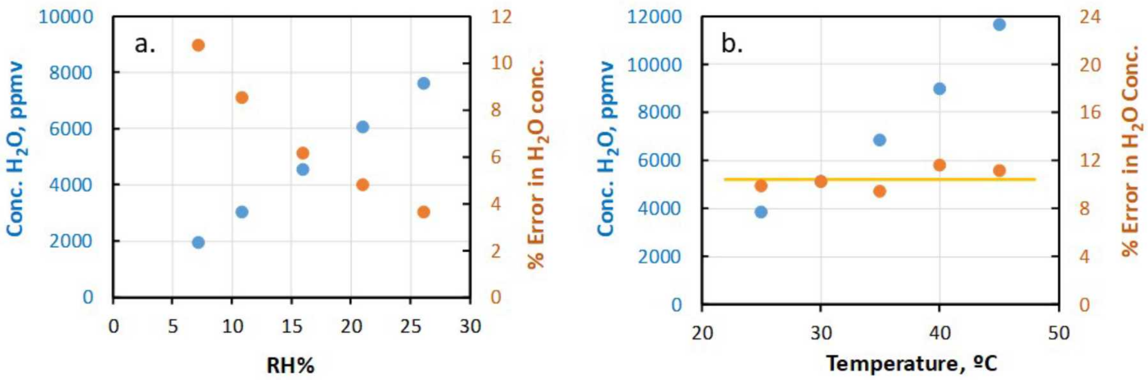

Figure 9. Estimating uncertainty in Vaisala probe measurements. a) Error in measured water content with increasing RH, constant temperature (21.1ºC); b) Error in measured water content with increasing temperature at constant RH (11.1 ± 0.1%)

4.2. Discussion

To summarize the water analysis data, the water content of Sample #1, collected five hours after drying, was qualitatively estimated to be 2000-2100 ppmv at ambient temperatures, similar to the value of approximately 1800 ppmv measured at the North Anna site. However, both of these are likely to be underestimates of the water present, because water adsorbed to the inside of the steel sample canister was not accounted for, and data from the Samples #2 and #3 show that adsorbed water can be a significant fraction of the total. Sample #2 was compromised during testing and some water was lost. The measured water content at ambient temperatures was ~6600 ppmv, much lower than the 10,000 ppmv measured at North Anna. With heating to 60-65ºC, however, the water content did rise to about 10,000 ppmv. Because of the lost water, this value represents a minimum water content for the cask gas phase, 5 days after completion of drying and backfilling. Analysis of Sample #3 yielded about 11,200 ppmv at ambient temperature, relatively consistent with the North Anna data. This increased with temperature, and stabilized at about 17,400 ppmv at 60-65ºC. The value of 17,400 ppmv, with an estimated uncertainty of ±10%, is the best estimate for the water content in the cask gas phase at the time of sampling, 12 days after drying and sealing the cask.

For both samples #2 and #3, the water content measured at ambient temperatures accounted for only 2/3 of the water present in the sample bottle, based on measurements after heating to 65ºC. This illustrates the importance of accounting for adsorbed water when quantifying water in a gas sample. Although the water content appeared to plateau above 60ºC for the Samples #2 and #3 (Figure 6 and Figure 7), additional adsorbed water may have been present. The low measured RH values at these temperatures suggest that any remaining adsorbed water is small.

An estimate of the amount of water in the gas phase within the demonstration cask requires knowledge of the total number of moles of gas present in the cask. This can be estimated using the ideal gas law. The volume of the gas phase is known (~5.4 m^3), as is the pressure (2.2 bars). Thermocouple readings within the cask show that the temperature of the cask internals varies significantly with location, as does that of the gas phase; the average gas temperature, after filling, has been estimated to be 183.4ºC. These values yield an estimated mass of gas present of 310.8 moles. Using this value, the measured water content of 17,400 ppmv ± 10% is equivalent to 97.4 ± 9.7 grams H_2O in the cask gas phase.

The measured water content for Sample #3 can be used to assess the possibility that liquid water is present in the high burnup demonstration cask. If the assumption is made that the gas phase in the cask is well-mixed, then if liquid water were present, it would be located at the coolest place in the cask, and the gas-phase water content would be equal to the saturated vapor pressure at the temperature of that location. In Figure 10, the saturated water content for air at a pressure of 2.2 bars is shown as a function of temperature. In order for the measured water content of 17,400 ppmv ± 10% to represent saturation in the cask, there would have to be a location in the cask that is at a temperature of 28±2ºC. Based on the thermocouple measurements and the thermal-hydraulic modeling that has been done, the coolest location in the cask is believed to be approximately 85ºC. At this temperature, 17,400 ppmv water content is equal to less than 10% RH. Hence, it is unlikely that there is any free water in the cask, unless it is trapped in an inaccessible location (e.g. within a rod) and is slowly bleeding out, or unless the assumption of a well-mixed, compositionally homogeneous gas phase is incorrect.

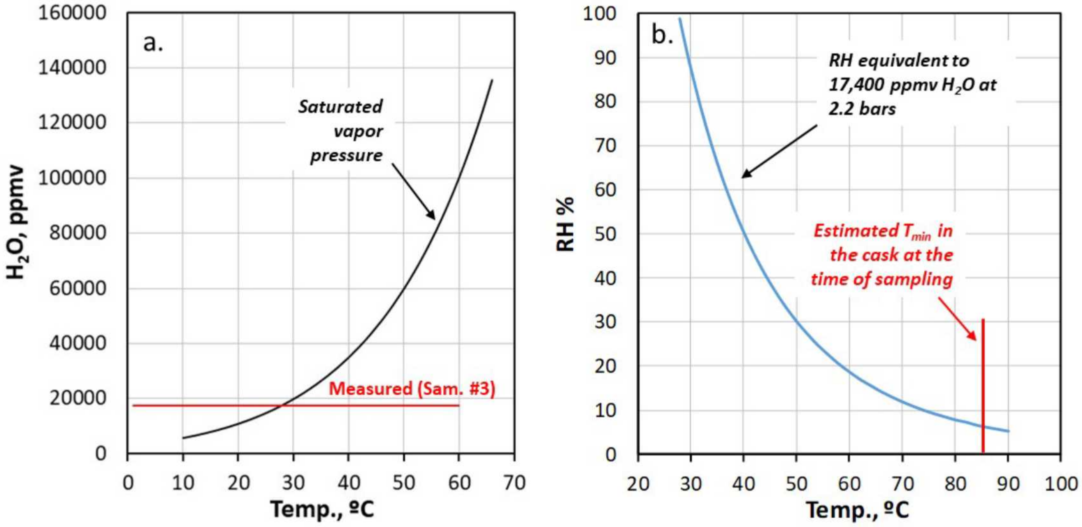

Figure 10. a) Saturated water content as a function of temperature at 2.2 bars total pressure. Red line indicates the measured value in Sample #3. b) The RH represented by the 17,400 ppmv H_2O, as a function of temperature. The anticipated coolest cask temperature at the time of sampling was about 85ºC.

4.3. Lessons Learned--Improved Measurement of Water Content in Dry Storage Canister Gas Samples

Several of the attempts to quantify water contents in the gas samples collected from the High Burn-Up Demonstration Cask were unsuccessful. However, they provide insights into how to improve future measurements. First, in order to quantify the water content properly, it is essential that the sample bottles be heated to desorb water adsorbed onto the interior of the bottles. In the case of the samples here, about 1/3 of the total water remained adsorbed to the metal at ambient temperatures. It follows, also, that the bottles must be must be pre-treated to remove any adsorbed water prior to use. Failure to dry the sample bottles before introducing the sample would result in measured water contents, upon heating, that are higher than the true value. Any gas lines connecting the sample bottle to the water detector must also be heated, and this is most consistently and readily accomplished by placing both the sample and the detector within a single oven. However, this limits the type of detection method that can be used.

While use of needle valves allowed long sample storage times without losing the sample, the needle valves also restricted flow to the point that flow through a loop configuration was not possible. If a consistent and rapid measurement method is available, such that long storage times are not necessary, it is recommended that full-open valves like ¼ turn plug valves be used on the sample bottles. This would allow recirculation through a loop, drastically reducing equilibration times for any in-line detector. Capacitance probes such as the Vaisala probe used here are available for use at temperatures over 100ºC, but have low accuracy at the low RH values anticipated to occur. In-line chilled mirror instruments are available that can be used at temperatures over 100ºC (for instance, the Mitchell S8000 Remote High Precision Chilled Mirror Hygrometer), and may be a good choice. It is important to remember that in a loop system, the volume of the sample has changed. Moreover, the surface area exposed to the sample gas has increased by the internal area of the loop tubing, and water sorption will rapidly occur onto the walls of the tubing. An accurate value for the gas water content requires heating the sample sufficiently to desorb all water from the walls of the sample bottle and loop, and also correcting for the change in sample volume.

An alternative approach would be to heat the sample, pump the gas through a cold finger to freeze out the water, and then to weigh it to determine the mass of water present. The feasibility of this method depends on the volume of the sample and the amount of water present. For a one-liter sample with the water concentrations measured here, quantification would require accurately measuring milligrams to a few tens of milligrams of weight change accurately.

Perhaps the most accurate approach would be to use an isotopic tracer—for instance, to inject microliter amounts of deuterated water (D_2O) into the sample bottle, to allow complete equilibration with water in the sample, and then to measure the $^2H/^1H$ ratio to determine the original amount of water present. This would require running blanks to assess the effect of exchange with hydroxyl groups on the metal surface (the metal surface is actually a thin metal oxide surface layer). Because it is possible to very accurately measure isotope ratios, the accuracy of this measurement would only be limited by the accuracy of the volume of tracer injected. Mechanical syringes capable of dispensing sub-microliter amounts of liquid are readily available (e.g., the Hamilton Company 7000 series syringes). Analysis could be accomplished by mass spectrometry or by use of a stand-alone instrument like the Los Gatos Research Water Vapor Isotope Analyzer used by Dominion Energy. Use of an isotope tracer has many advantages. Heating during analysis is no longer necessary, so long as the sample is well-equilibrated with the tracer. Once adsorbed water is in isotopic equilibrium with water in the gas phase, there is no need to desorb water by heating, since the isotope ratio of the water is present in the gas phase can be used to calculate the total water content. Heating prior to analysis might be used to speed equilibration with adsorbed water, but given sufficiently long equilibration times, it is not necessary.

5. CONCLUSIONS

To summarize, one-liter gas samples were taken from the High Burn-Up Demonstration Cask at three intervals: 5 hours, 5 days, and 12 days after the completion of drying and backfilling. The samples were analyzed for water content at ambient temperatures at North Anna, and a second set of the samples, was shipped to Sandia National Laboratories for more complete analysis. Samples were initially counted using gamma-ray spectroscopy (400,000 second count) to determine if fission gases were present, focusing on ^{85}Kr, for which gamma spectroscopy is highly sensitive. No ^{85}Kr was observed in any of the samples. Gas aliquots were then analyzed for water content, and by direct gas mass spectrometry to determine non-sorbing gases. The mass spectrometric analysis provided concentrations of non-sorbing gases in the samples. Several important trends were observed, including increases in CO_2 up to 930 ppmv and H_2 up to nearly 500 ppmv after two weeks of storage. Trace amounts of organic compounds were also observed. We hypothesize that the CO_2 was generated by reactions between a hydrocarbon contaminant (possibly vacuum grease used on the pump fittings or vacuum pump oil) and oxidizing species produced by water radiolysis. Increasing H_2 concentrations may also be due to radiolysis, followed by consumption of the accompanying oxidizing species by oxidation of the organic material or by metal corrosion. However, if anoxic conditions exist in the cask, H_2 may also be produced by direct reduction of water by metals in the cask.

To measure water content, a Vaisala humidity probe was used and the sample was heated in steps to desorb water adsorbed to the bottle interior. Heating proved to be critical for accurate water quantification; the water content measured at ambient temperature was only $^2/_3$ of the total water measured at 65ºC. Final results indicated that the cask gas water content built up over 12 days to a value of 17,400 ppmv ±10%, equivalent to approximately 100 g of water within the entire cask gas phase. The measured water content corresponds to less than 10% relative humidity at 85ºC, the minimum anticipated temperature in the cask at the time of sampling. If the cask gas phase is compositionally homogeneous, then liquid water is not present within the cask, unless trapped in inaccessible locations.

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