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LOW-TEMPERATURE, VACUUM-ASSISTED DRYING OF DEGRADED SPENT NUCLEAR FUEL

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ABSTRACT

A variety of legacy, spent nuclear fuel, wastes are stored in below-grade, vertical, cylindrical, steel and concrete structures called “tile holes” in Waste Management Areas (WMAs) at the Chalk River Laboratories (CRL) site. Inspections have revealed the presence of moisture in some of the tile holes, contributing to corrosion of the fuel-storage containers and fuel itself. A major fuel remediation initiative, the Fuel Packaging & Storage (FPS) Project, has been initiated to remediate the legacy fuels at CRL. The objective of the FPS Project is to stabilize the fuels by removing moisture and storing the fuel in a controlled atmosphere to reduce fuel corrosion and deterioration, such that future hazards and costs of handling the fuel are minimized.

A low-temperature (<100°C), vacuum-assisted-drying process, commonly known as Cold Vacuum Drying (CVD), has been evaluated for drying CRL legacy fuel. A test program has been conducted to assess the drying characteristics of CRL legacy fuels under CVD conditions using samples obtained from a legacy-fuel storage container retrieved from the WMAs at CRL. This paper describes the proposed CVD process, the drying tests and discusses the implication of the observed drying characteristics of corroded fuel samples on full-scale drying of CRL legacy fuel.

BACKGROUND

AECL has operated research reactors at the CRL site since 1947, for the purpose of nuclear energy and scientific research and for the production of radioisotopes. During the 1950s and 60s, a variety of spent nuclear fuel wastes were produced by irradiating metallic uranium and other prototype fuels. These legacy waste fuels were initially stored in water-filled fuel storage bays for a period of several years before being placed in mild steel storage containers and transferred to the CRL Waste Management Areas (WMAs), where they have since been stored in below-grade, vertical, cylindrical, steel and concrete structures called “tile holes”.

Field investigations have revealed the presence of water in some of the tile holes. In some cases, this resulted from incomplete water removal when the storage cans were taken out of the original water-filled fuel storage bay. There has also been ingress of surface water into some tile holes, through degraded flange gaskets. Another source of moisture has been environmental humidity entering the tile holes, resulting in condensation and a net accumulation of moisture over time. Over the years, this has led to the corrosion of the aluminum flow tubes, cladding and fuel itself, in particular, uranium metal fuels. These fuels need to be stabilized by removing the moisture and storing them in controlled, dry atmospheres to reduce further deterioration. This would reduce the future hazards and minimize future fuel handling costs. A major fuel remediation initiative, the Fuel Packaging & Storage (FPS) Project, has been initiated to remediate the legacy fuels at CRL. More details of the FPS Project can be found in Reference 1.

Fuel Description

Under humid conditions in the tile holes, aluminum-clad, uranium-metal fuels are the most susceptible to corrosion degradation. When all fuel rod materials are considered, the aluminum-clad metallic uranium fuel rods represent the highest priority when considering protection of the environment and risks to health and safety of workers and the public. Continued corrosion of this fuel can be expected to significantly increase the future costs and hazards for handling the fuel and decommissioning the CRL tile holes. As a consequence, the FPS-scope fuels (Table 1) essentially consist of metallic uranium and uranium dioxide, both clad in aluminum having less corrosion resistance than modern alloy-clad uranium oxide fuels. A small fraction of the FPS-scope fuels also include thorium metal, uranium carbide and uranium-aluminum alloy rods.

TABLE 1: Legacy Fuels to be Remediated by the Fuel Packaging & Storage Project

Fuel Type	Percent of Total (22 tonnes)	Cladding Material
Uranium Metal (flat rods)	56	Aluminum
Uranium Dioxide Annular or Solid Rods	34	Aluminum
Thorium Metal	5.6	Aluminum
Uranium-Aluminum Alloy	<1	Aluminum
Uranium-Zirconium Alloy	2.5	Aluminum
Thorium-Uranium Mixed Oxide	1.5	Zircaloy
Uranium Carbide	<1	304 Stainless Steel

Types of Water Present in the Storage System

The nature and the extent of the corrosion products present determine the drying characteristics of waste fuels. Consequently, the drying characteristics of corroded aluminum-clad, uranium metallic fuel are likely to bound the drying characteristics of FPS-scope fuel listed in Table 1. A wide spectrum of corrosion products of uranium, aluminum and iron are expected to be present in storage containers containing uranium-metal fuels that were exposed to humid conditions [2]. The uranium oxides can include simple uranium oxides (UO_2, U_4O_9, U_3O_7 and U_3O_8) and hydrates such as, $UO_2(OH)2$, $UO_4.4H_2O$, $UO_4.2H_2O$ etc. Aluminum and iron corrosion products can include polymorphs of aluminum ($Al(OH)_3$ and AlOOH) and iron ($Fe(OH)_3$ and FeOOH). The nature and the composition of the corrosion products are expected to depend on the corrosion conditions.

In addition to the free water that may be present, water can also be present in corrosion products as chemisorbed (hydration water and hydroxyls) and physisorbed water in storage containers containing legacy fuels (Historic Storage Containers (HSC)). While the water content associated with hydrates depends only on the quantity of the hydrates present, the amount of physisorbed water depends on the quantity, surface area and porosity of the corrosion products, and the relative humidity. The equilibrium water vapor pressure, which is a key parameter of interest for drying operations associated with corrosion products, is bounded by the saturated water vapor pressure curve, except for $Fe(OH)_3$, which is unstable in ambient air (stable only in liquid water) [2].

Physical adsorption of water on surfaces involves relatively weak intermolecular forces and consequently, physisorbed water can be removed under relatively mild conditions (<100ºC and vacuum) [2]. Forces binding chemisorbed water and water of hydration are strong and as a consequence, relatively high temperatures (>100ºC) are generally required to release them. Although the proposed CVD is designed to remove only the free water, a large fraction of the physisorbed water is also expected to be removed during CVD.

Fuel Drying

A key objective of the FPS Project is to use proven techniques and equipment for fuel drying. The CVD process proposed for the FPS Project is conceptually similar to the CVD process currently being used for drying N-reactor fuel at the United States Department of Energy (DOE) Hanford Site [3].

In the FPS project, fuel drying will take place inside a purpose-built overbuilding. The HSCs will be retrieved from the tile holes and transferred in a transfer flask, one at a time. They will be repackaged, without removing the fuel from the HSCs, and dried inside a Packaging and Drying Station (P&DS). The dried fuel will be moved into a monitored storage vault.

A conceptual schematic of the P&DS is shown in Figure 1. The P&DS essentially consist of a Vacuum Vessel inserted into a cylindrical concrete and steel structure. The vacuum drying equipment is connected to the vacuum vessel. The HSCs will be repackaged into new, vented, stainless steel containers (FPS Storage Containers (FPS-SCs)) that will be located inside the Vacuum Vessel, without further processing (sorting, cutting, removing sludge or cleaning). After packaging operations are completed, the isolation valve will be closed, system leak checked and the vacuum vessel pressurized with an inert gas (argon or helium) to 1 (one) atmosphere and heated to the operating temperature (<100°C) with circulating hot water through an external heating jacket in the

Vacuum Vessel. The vacuum drying process begins when the complete system reaches the operating temperature.

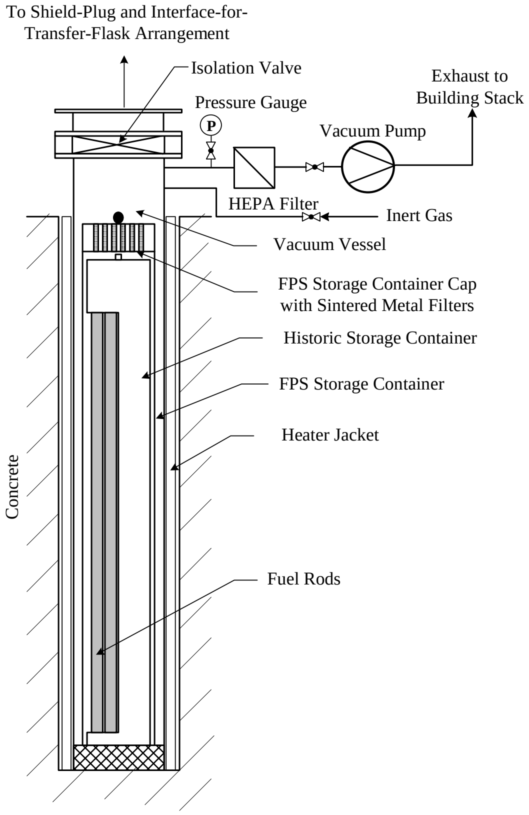

Figure 1 - Vacuum Drying System

In the vessel-in-vessel design used (Figure 1), heat transfer from the heating jacket to the fuel materials inside the HSC can be expected to be poor during CVD. Poor heat transfer to water can lead to water freezing, slowing the drying process. Consequently, a CVD process with periodic heating cycles is used to maintain practical drying rates. Frozen water is thawed simply by pressurizing the Vacuum Vessel with an inert gas to facilitate heat transfer.

As previously noted, the CVD process is designed to remove primarily free water present in the fuel materials. Therefore, after the CVD process, chemisorbed and some physisorbed water are expected to remain in the fuel materials.

Two factors complicate the FPS-scope-fuel drying process. First, the fuels are old (over 40 years in storage) and they are relatively cold with an average decay power of ~4 W/HSC. The second, as already discussed, is the presence of corroded fuel with exposed reactive uranium metal. Uranium metal reacts with air, water or water vapor exothermally, according to reactions 1 and 2 [4].

$$U + 2\,H_2O_{\text{liquid or vapor}} \rightarrow UO_2 + 2H_2 \qquad (1)$$

$$U + O_2 \rightarrow UO_2 \qquad (2)$$

During drying of uranium metal fuel under vacuum, the heat released in the presence of water or water vapor can increase the temperature of the fuel, if not rejected at a sufficient rate. This increase in the fuel temperature, in turn, leads to an increase in the reaction rates causing thermal excursions in fuel with the potential for thermal runaway. The potential for thermal excursions in uranium metallic fuel during drying increases with the operating temperature and is the basis for choosing a low-temperature (<100°C) vacuum drying process for drying FPS-scope fuel.

Long-Term Storage

After CVD, the FPS-SCs will be pressurized with an inert gas and moved from the P&DS to monitored stainless steel Storage Tubes located in the above ground concrete Storage Block inside the overbuilding. A conceptual schematic of the dried fuel storage arrangement is shown in Figure 2. After inserting the shield plug, the Storage Tube will be closed with a top flange, providing a leak-tight enclosure to the FPS-SC, and pressurized with a suitable cover gas, still to be determined. The top flange will be equipped with a pressure gauge for continuous monitoring of the pressure in the space above the FPS-SC. In addition, a sampling line is provided to sample the gas in the space above the FPS-SC for analysis. The pressure and the cover-gas composition will continue to be monitored during storage, to assess the condition of the fuel during storage.

Uranium-metal/water corrosion rate (Equation 1) has been found to be significantly higher in O_2-free (anoxic) atmospheres (<100 ppm of O_2), compared to O_2-containing (oxic) atmospheres [5]. Anoxic conditions, also, promote the formation of H_2 and UH_3 according to reactions 3 and 4.

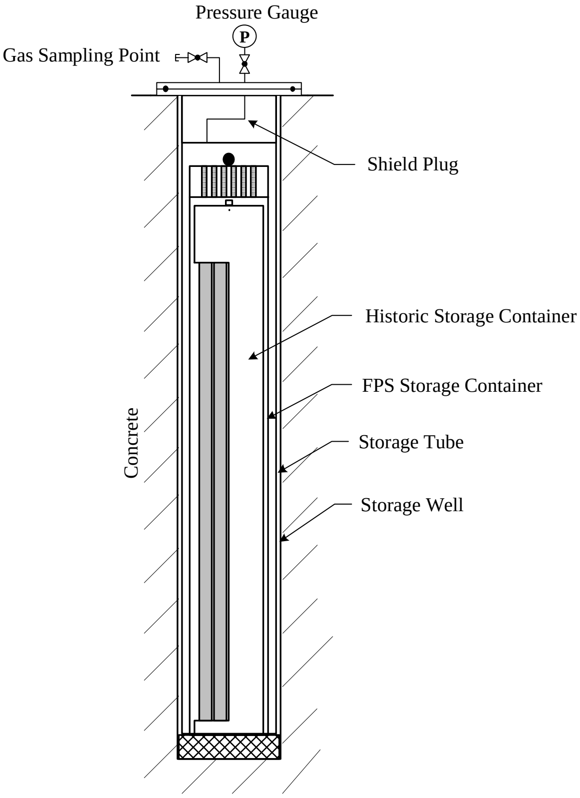

Figure 2 - Dried Fuel Storage Arrangement

$$4U + 4\,H_2O_{\text{liquid or vapor}} \rightarrow 2UH_3 + 2UO_2 + H_2 \qquad (3)$$
$$2U + 3\,H_2 \rightarrow 2UH_3 \qquad (4)$$

Consequently, a cover gas rich in O_2 is considered more suitable for use during long-term storage under monitored conditions. However, in an O_2-rich atmosphere, the residual water left after CVD will remain largely unaffected. In an O_2-free atmosphere, the residual water left after CVD will be consumed according to Reaction 3, further dehydrating the fuel materials with time during storage. The dried fuel performance characteristics under different cover gases with and without O_2 are currently being investigated to determine a suitable option for long-term storage.

FUEL DRYING TESTS

A test program has been conducted to assess the drying characteristics of CRL legacy fuels and to establish suitable drying-process parameters and a CVD-termination criterion.

A 23-cm diameter and 3.5-m long HSC containing five, 62 kg, trace-irradiated (near-contact radiation field measurements, were 80 $mR.h^{-1}$ in the middle, 30-50 $mR.h^{-1}$ near the top and 40 $mR.h^{-1}$ near the bottom of the can) aluminum-clad, natural uranium-metal fuel rods, was chosen for this study. This HSC was chosen because the fuel was known to be severely corroded, and its drying characteristics are expected to bound the drying characteristics of all the fuel material types comprising the FPS project scope.

The HSC, as-retrieved, did not contain free water. Relatively little corrosion was observed at the top of the HSC, while the extent of corrosion was found to be extensive at the bottom of the can. This appears to suggest a much more humid environment at the bottom of the HSC during tile-hole storage. In addition, a ~1.2-m long bitumen deposit was found to be present inside the HSC, adding an extra variable to the drying process. In some tile holes, after emplacement of a HSC, the space between the HSC and the tile hole was packed with sand and bitumen poured to seal off the top, to stop water ingress into the tile holes. However, in this particular case, bitumen appeared to have seeped through the sand plug, likely due to poor compaction, filling the voids.

A total of five, 25-cm long, full cross-section samples along the length of the HSC were cut and packaged into separate drying-test containers. The 30-cm high, drying-test containers are O-ring sealed, flanged vessels constructed of 25-cm diameter, schedule 40, stainless steel pipe. The test containers were helium leak tight to below 1 x10^{-6} $cm^3.s^{-1}$. The drying-test samples are shown in Figure 3. Significantly more corrosion products were found in test samples obtained from the bottom of the HSC than from the top.

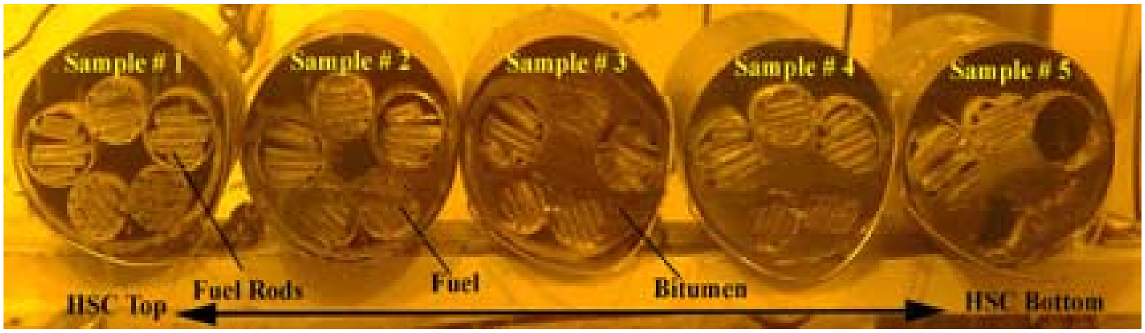

Figure 3 – Drying-Test Samples

The intent of the proposed CVD process for FPS-scope fuel is to remove residual free water from the HSCs, and this can be demonstrated by measuring the equilibrium-water-vapor pressure inside the vacuum vessel after CVD. A simple pressure measurement can be used to establish the equilibrium water vapor pressure assuming that the measured pressure inside the vacuum vessel is due only to water vapor. Even if other gases were present, a pressure measurement lower than the saturated water vapor pressure would be a clear indication for the absence of free water in the HSC. Although a quantitative estimate of the extent of the dehydration of fuel materials cannot be made following CVD, an equilibrium pressure measurement can be used to qualitatively establish the extent of dehydration. The lower the equilibrium pressure, the higher the extent of dehydration. When corrosion products are present, establishing equilibrium between water vapor in the gas and adsorbed phases can be a slow process. Consequently, equilibrium pressure measurements can only be effective as a final measure to terminate the CVD process. A faster means of measurement, therefore, may be needed to establish the extent of dehydration during CVD process.

The DOE-Hanford CVD process uses a pressure-rebound test to establish the CVD process termination point [6]. A pressure-rebound test is initiated, when the pressure inside the drying vessel is below ~0.67 kPa, by isolating the drying vessel and measuring the rate of pressure rise inside the vessel for 1 h. The rate of pressure rise has been shown to correlate with the amount of water present in fuel cracks and a pressure-rise rate <0.39 kPa/h is used to terminate CVD. During CVD tests, pressure-rebound tests were performed to assess whether a pressure-rebound rate can be established experimentally, to determine the extent of dehydration, before a final equilibrium pressure measurement is made to terminate the CVD process.

Experimental Set-up

A schematic of the experimental set-up is shown in Figure 4. The test set-up essentially consisted of three subsystems:

1. An inert feed gas (commercial grade helium) system with humidification capability;
2. An instrumented drying-test container; and
3. A vacuum system.

Helium gas was used to humidify the fuel materials before the drying tests and as the heating medium in the event ice is formed inside the drying container during CVD. The humidity of the gas stream at the inlet and outlet of the drying vessel was measured with Panametrics, Al_2O_3 moisture probes (-80°C - +60°C dew point range).

The drying container and associated vacuum system were instrumented to measure the temperature (type K thermocouples) and pressure (MKS pressure transducers). The inlet and outlet ports of the test container were equipped with 2-µm, high surface area particulate filters to arrest particle migration during CVD. The test container was mounted on a Satorius bench scale (0 – 150 kg with ±10 g resolution) to dynamically measure the weight gain and loss during the tests. The wall of the insulated vessel was heated and maintained at the desired operating temperature (50 or 75ºC) using an externally mounted electrical heater (1.5 kW), with a built-in on-off-type temperature controller and a Type K thermocouple. All process lines, with potential for moisture condensation during the drying tests, were heated to ~50ºC using wrap-on heating tape, and Variac and type-K thermocouples.

The vacuum system consisted of a Varian, Triscroll 300 (250 $L.s^{-1}$), dry scroll vacuum pump and a Varian liquid nitrogen (LN_2) cold trap, to protect the pump against moisture. In addition to the protection of the vacuum pump against moisture, the water collected in the cold trap also provided a quantitative estimate of the water removed from the fuel during CVD. The pump inlet pressure was monitored using a Piezo/Pirani dual-pressure transducer.

The data from all instruments, except for the Satorius bench scale, were handled using a 16-channel Eurotherm data logger. The data from the Satorius bench scale were handled using a personal computer based data acquisition, display and storage system. The experimental system was located inside a fumehood and a photograph of the part of the experimental set-up located inside the fumehood is shown in Figure 5.

Before an experiment, the complete system was helium leak-tested to ensure that the leak rates are below 1×10^{-5} $cm^3.s^{-1,}$ using a helium leak sniffer. A typical experiment started by first humidifying the fuel materials in the drying-test container with a 90-95% Relative Humidity helium stream for ~5 h. After humidifying the fuel materials, a known amount of water (50-200 g) was injected into the test container through the injection port and the container was left overnight (~15 h) allowing the water vapor to equilibrate with the fuel materials.

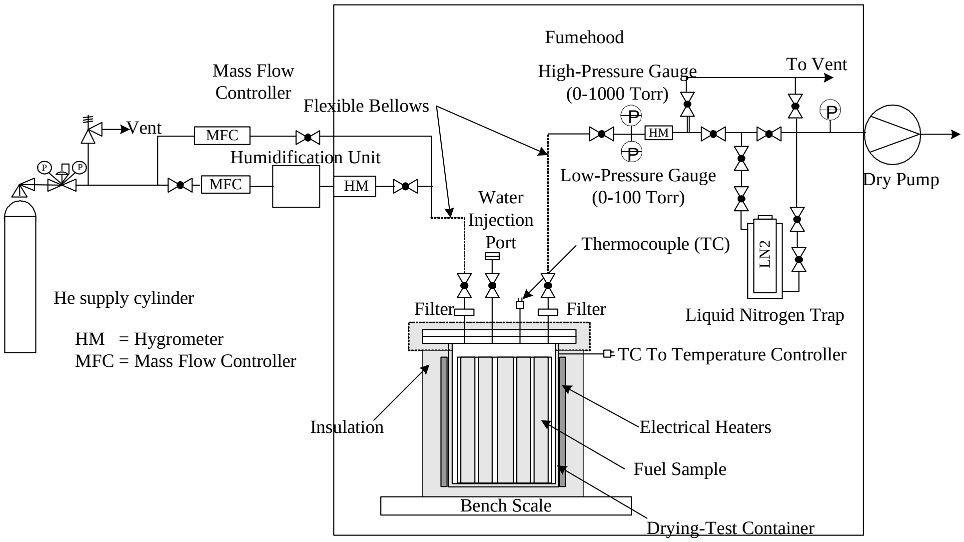

Figure 4 – Simplified Schematic of the Experimental System (1 Torr = 0.133 kPa)

Before the drying tests, the drying-test container was heated to the operating temperature (50 or 75ºC) and the liquid-nitrogen trap was cooled to 77 K. The drying tests were started first by zeroing the bench scale and by opening the drying test container to the vacuum pump after closing the appropriate valves. Heating cycles (~0.5 h) were initiated when the pressure approached a low limiting value. A pressure-rebound test was normally performed before a heating cycle. At the end of a working day, the drying-test container was allowed to cool down to ambient temperature overnight, to minimize interference from other desorbing gases, to measure the equilibrium pressure. The drying test was usually terminated when the measured pressure was significantly below the saturated water vapor pressure at ambient temperature.

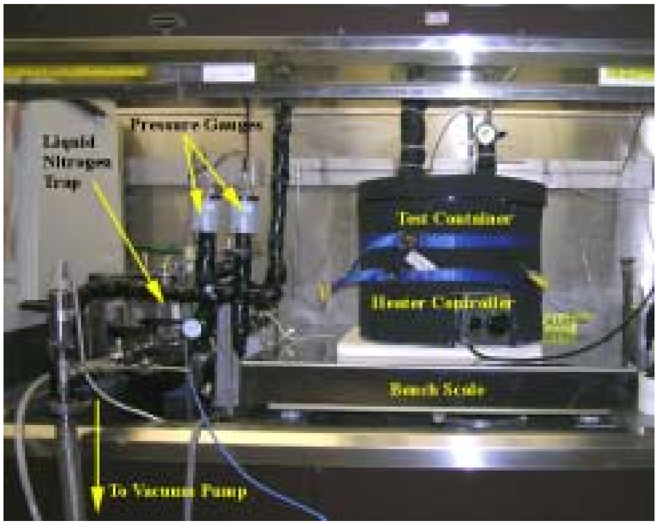

Figure 5 – Experimental System

Results and Discussion

Before CVD tests were conducted with actual fuel samples, the effect of water freezing under poor heat transfer conditions on water removal characteristics, was investigated in the temperature range 50 to 75ºC. These tests used a plastic container, filled with 100 g of water, placed inside an empty drying-test vessel to simulate poor heat transfer conditions that may exist during CVD of fuel materials. Figure 6 shows the water freezing characteristics during CVD at 50ºC. As can be seen in Figure 6, the water temperature decreases sharply, as the pressure inside the test container is lowered during CVD, leading to freezing. Both the weight loss and pressure reach limiting values as water is frozen. As the data show, poor heat transfer conditions that may prevail during CVD, can lead to poor drying rates. While, this example represents an extreme case and the heated fuel mass in the HSC is available to supply the heat of evaporation to the water during CVD, poor heat transfer conditions may still exist for water that is trapped within corrosion products and could lead to water freezing.

Typical weight loss and, pressure and temperature characteristics observed during CVD tests are shown in Figures 7 and 8 respectively. A typical CVD cycle consisted of heating the drying-test container to the operating temperature under helium, evacuating the container until pressure reaches a low limiting value followed by a pressure-rebound test (see Figure 8).

As-received fuel samples did not contain free water. This was further confirmed by equilibrium pressure measurements inside drying-test containers before the tests. Significantly more water was recovered from the fuel samples, than injected from fuel samples obtained from the bottom of the HSC. These data are consistent with the presence of physisorbed water in corrosion products and the observation that there were significantly more corrosion products at the bottom of the HSC than at the top. The equilibrium pressure measurements made at ambient temperature, following termination of CVD, were found to be generally significantly lower than the saturated water vapor pressure, indicating that the CVD process is capable of removing not only free water, but

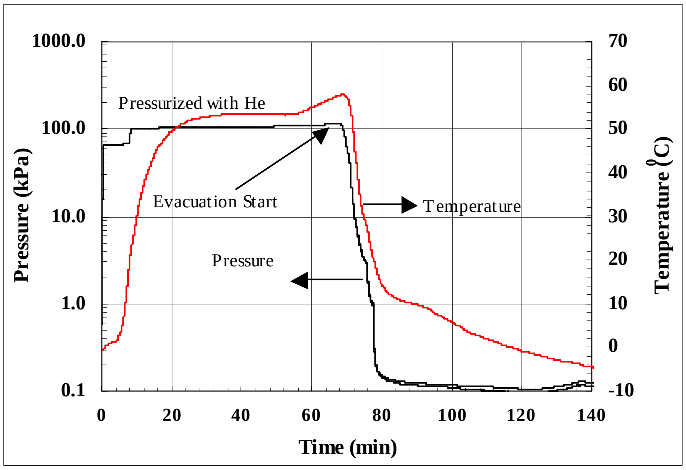

Figure 6 – Water Freezing Characteristics Inside a Plastic Container During CVD

also the physisorbed water. This is also consistent with the fact that more water than injected, as free water, was recovered from fuel during CVD.

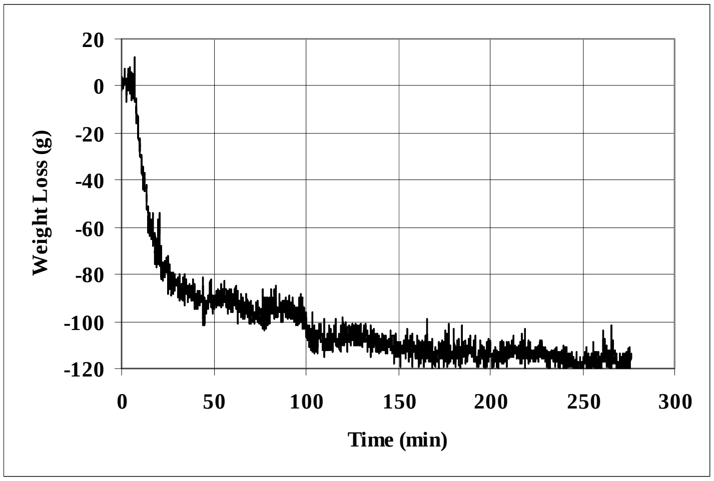

Figure 7 – Weight Loss Curve (50°C, 100 g Water)

Periodic pressure-rebound measurements, made during CVD tests, failed to produce a correlation between the pressure-rebound rate and the extent of fuel dehydration. Hydrogen was found in the gas phase following pressure-rebound tests at 75°C. Hydrogen production from corrosion reactions (see Equation 1) can obscure the pressure rise due to water vapor during pressure-rebound tests. This effect is expected to increase with increasing temperature and exposed uranium surface area. This may have contributed to the observed lack of correlation between the pressure-rebound rate and the extent of fuel dehydration.

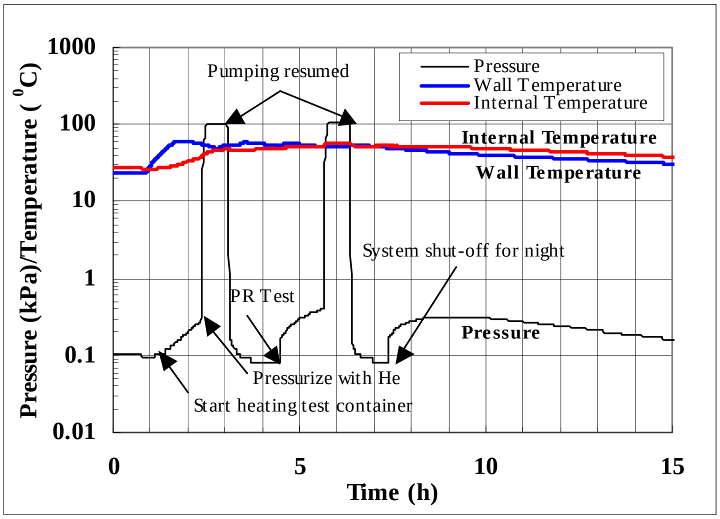

Figure 8 – Cyclic CVD Process (PR Test = Pressure-Rebound Test)

Bitumen was found to start to melt around 75ºC and melt completely at 100ºC. Melting of bitumen can potentially restrict access to water in fuel materials, inside the HSC, during CVD. Consequently, temperatures below 75ºC may need to be considered for drying HSCs that are likely to contain bitumen. Degassing experiments showed that mainly water was released from bitumen at temperatures below 75ºC. Only trace amounts of H_2, CO_2 and organics were found in the gases evolved. The amount of H_2 in the gases evolved reached ~20% at 100ºC. The mass of bitumen lost during degassing tests was found to be <1% up to 100ºC making bitumen a negligible source of water inside HSCs.

LONG-TERM SAMPLE STORAGE

The five drying-test containers that were subjected to CVD tests are currently stored under a cover gas containing 2% O_2 in argon. The ambient temperature inside the enclosure containing the test containers and the pressure inside the test containers are shown in Figure 10 for two containers before and after drying. When the pressure inside the containers increases above 5 psig, the containers are purged with 2% O_2 in argon gas and re-pressurized to ~1-2 psig, as a precautionary measure. As the data show, before drying, relatively sharp pressure increases with time are seen in the two containers. After drying, no significant pressure increases were noted. These data appear to indicate that the post-CVD fuel materials are more dehydrated than the as-received materials. These data are still preliminary and long-term post-CVD-fuel-monitoring tests will be ongoing for a period of several months.

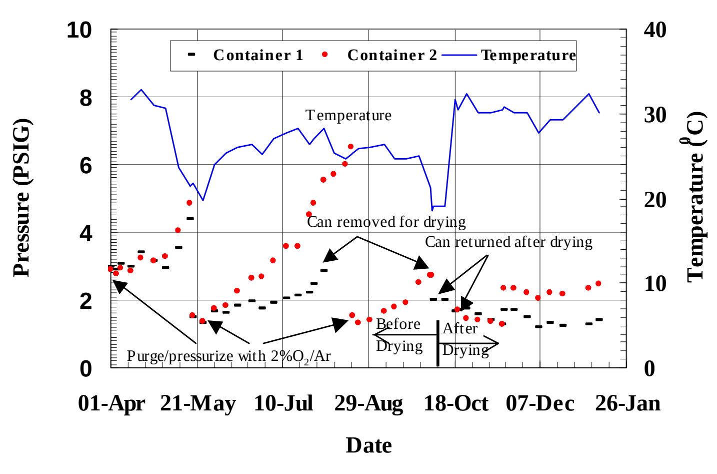

Figure 9 – Pressure Behaviour in Drying Test Containers During Storage (1 PSI = 6.89 kPa)

SUMMARY AND CONCLUSIONS

The CVD process will be used for drying CRL legacy fuels. The intent of the CVD process is to remove primarily free water present in the fuel materials. After CVD, chemisorbed and some physisorbed water are expected to remain in the fuel materials. The dried fuel will be subsequently stored in an above ground storage system, in which the dried fuel will be kept under controlled, dry, atmospheres that will be monitored.

Fuel drying tests have been performed to demonstrate the proposed CVD process. The CVD process was shown to be capable of removing free water from fuel completely, in addition to some of the physisorbed water. Although the test samples did not contain free water, before drying, relatively sharp increases in pressures were seen in drying-test containers maintained under controlled atmospheres. After CVD, no significant pressure increases were noted, suggesting that the post-CVD fuel materials are significantly more dehydrated than the as-received materials, and indicating an effective CVD process.

Extraneous materials, such as bitumen that is expected to be present in some HSCs, are likely to be an insignificant source of water. However, the presence of bitumen may limit the CVD temperature to ~50ºC in order to avoid melting.

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