Pacific Northwest National Laboratory

Operated by Battelle for the
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Drying Results of K-Basin Fuel Element 0309M (Run 3)

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July 1998

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

An N-Reactor outer fuel element that had been stored underwater in the Hanford 100 Area K-West Basin was subjected to a combination of low- and high-temperature vacuum drying treatments. These studies are part of a series of tests being conducted by Pacific Northwest National Laboratory on the drying behavior of spent nuclear fuel elements removed from both the K-West and K-East Basins.

The drying test series was designed to test fuel elements that ranged from intact to severely damaged. The fuel element discussed in this report was removed from K-West canister 0309M during the second fuel selection campaign, conducted in 1996, and has remained in wet storage in the Postirradiation Testing Laboratory (PTL, 327 Building) since that time. The fuel element was broken in two pieces, with a relatively clean fracture, and the larger piece was tested. A gray/white coating was observed. This was the first test of a damaged fuel element in the furnace. K-West canisters can hold up to seven complete fuel assemblies, but, for purposes of this report, the element tested here is designated as Element 0309M.

The drying test was conducted in the Whole Element Furnace Testing System located in G-Cell within the PTL. The test system is composed of three basic systems: the in-cell furnace equipment, the system gas loop, and the analytical instrument package. Element 0309M was subjected to drying processes based on those proposed under the Integrated Process Strategy, which included a hot drying step. The test cycles are listed below:

- Cold Vacuum Drying (CVD) at $\sim 50^{\circ}\text{C}$ under vacuum (~ 0.7 hr)
- Pressure Rise Tests (2) at $\sim 50^{\circ}\text{C}$ (~ 2 hr)
- Hot Vacuum Drying (HVD) for a total of 59 hr (~ 17 hr at $\sim 80^{\circ}\text{C}$, ~ 34 hr at $\sim 80^{\circ}\text{C}$ to $\sim 400^{\circ}\text{C}$, and ~ 8 hr at $\sim 400^{\circ}\text{C}$)
- System Cooldown to $\sim 50^{\circ}\text{C}$ (~ 29 hr)
- Post-Test Pressure Rise Test at $\sim 50^{\circ}\text{C}$ (~ 1 hr).

Approximately 5 ml of water were observed in the condenser during the condenser pumpdown phase of CVD. Two Pressure Rise Tests were conducted following CVD. The first Pressure Rise Test did not meet the criterion of <0.6 Torr/hr and, therefore, a second test was successfully conducted. Approximately 4 mg of water were removed during both Pressure Rise Tests, likely from *free* water, trapped under the observed surface coating on the fuel element, which was not completely released during CVD.

Approximately 2 g of water were released during HVD, with the largest amount (~ 1.7 g) removed during the temperature increment from $\sim 80^{\circ}\text{C}$ to $\sim 400^{\circ}\text{C}$. Thermal decomposition of hydrated species was significant in controlling the removal of water from the system during the HVD. As a result, a temperature above 400°C may be required for complete drying of the hydrated species within a reasonable period of time.

Hydrogen was also observed during HVD starting at about 150°C. Two main peaks were evident, at ~222°C from oxidation of the fuel by water, and at ~270°C from the decomposition of uranium hydride. Total hydrogen release during HVD was ~19 mg.

Quality Assurance

This work was conducted under the Quality Assurance Program, Pacific Northwest National Laboratory (PNNL) SNF-70-001, *SNF Quality Assurance Program*, as implemented by the PNNL *SNF Characterization Project Operations Manual*. This QA program has been evaluated and determined to effectively implement the requirements of DOE RW-0333P, Office of Civilian Radioactive Waste Management *Quality Assurance Requirements and Description (QARD)*. Compliance with the QARD is mandatory for projects which generate data used to support the development of a permanent High-Level Nuclear Waste repository. Further, the U.S. Department of Energy has determined that the testing activities which generated the results documented in this report shall comply with the QARD. Supporting records for the data in this report are located in the permanent PNNL SNF Characterization Project records, *Furnace Testing of SNF Fuel Element 0309M*.

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Acronyms

ATS	Applied Test Systems
CVD	Cold Vacuum Drying
DACS	data acquisition and control system
ET	elapsed time
GC	gas chromatograph
HP	Hewlett Packard
HVD	Hot Vacuum Drying
ID	inside diameter
IPS	Integrated Process Strategy
MS	mass spectrometer
NIST	National Institute of Standards and Technology
OD	outside diameter
PNNL	Pacific Northwest National Laboratory
PTL	Postirradiation Testing Laboratory
QA	Quality Assurance
QARD	Quality Assurance Requirements and Description
SFEC	single fuel element canister
SNF	spent nuclear fuel
UHP	ultra high purity
VP	vapor pressure
XRD	X-ray diffraction

1.0 Introduction

The water-filled K-Basins in the Hanford 100-Area have been used to store N-Reactor spent nuclear fuel (SNF) since the 1970s. Because some leaks in the basins have been detected and some of the fuel is breached due to handling damage and corrosion, efforts are underway to remove the fuel elements from wet storage. An Integrated Process Strategy (IPS) has been developed to package, dry, transport, and store these metallic uranium spent nuclear fuels in an interim storage facility on the Hanford Site (WHC 1995). Information required to support the development of the drying processes, and the required safety analyses, is being obtained from characterization tests conducted on fuel elements removed from the K-Basins. A series of whole element drying tests (reported in separate documents, see Section 8.0) have been conducted by Pacific Northwest National Laboratory (PNNL)^(a) on several intact and damaged fuel elements recovered from both the K-East and K-West Basins.

This report documents the results of the third of those tests, which was conducted on an N-Reactor outer fuel element removed from the K-West canister 0309M. This element (referred to as Element 0309M) was stored underwater in the K-West Basin from 1983 until 1996. Element 0309M was subjected to a combination of low- and high-temperature vacuum drying treatments that were intended to mimic, wherever possible, the fuel treatment strategies of the IPS. The system used for the drying test was the Whole Element Furnace Testing System, described in Section 2.0, located in the Postirradiation Testing Laboratory (PTL, 327 Building). The test conditions and methodologies are given in Section 3.0. Visual inspections on the fuel element (both pre-test and post-test) and the experimental results are provided in Sections 4.0 and 5.0. These results are further discussed in Section 6.0.

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2.0 Whole Element Furnace Testing System

A complete description for the Whole Element Furnace Testing System, including detailed equipment specifications, is provided in Ritter et al. (1998).

2.1 Major Systems Overview

An overview of the furnace testing system is presented in this section. The subsystems pertinent to this test report are as follows:

- **Vacuum Pumping System**—This system consists of a scroll-type vacuum pump, a condenser with chiller, filters, valves, and piping, which provide the vacuum pressures and flows required for the proposed IPS vacuum processes.
- **Process Heating System**—This system consists of a resistively heated, clam-shell furnace and a sample chamber (retort) to provide heating to the fuel element and to control process temperatures.
- **Gas Supply/Distribution System**—This system consists of gas bottles; mass flow controllers; piping; and valves for metering argon, air, or oxygen through the system. A bubbler is also available for adding water vapor to the system if desired.
- **Gas Analysis Instrumentation**—The gas analysis instrumentation includes a 300-amu quadrupole mass spectrometer (MS) and a gas chromatograph (GC) for monitoring selected elements in the process gas stream.
- **Process Instrumentation**—The system is equipped with several instruments for measuring process temperatures, pressures, and moisture level. An auxiliary turbo vacuum pumping system provides low system pressures for zero adjustment of the high accuracy retort pressure sensor.
- **Data Acquisition and Control System (DACS)**—The DACS consists of a IBM-compatible computer and data acquisition/control unit to monitor/store key system parameters (temperatures, pressures, flows, moisture level), along with controlling the process heating system and a safety argon system.

Figures 2.1 and 2.2 are photographs of the equipment located inside and outside of the PTL G-Cell. The furnace (including retort) and some of the process piping, instrumentation, and valves are located inside the hot cell. The furnace sits on the cell floor, and the process piping is routed to a rack that hangs on the west cell wall. Process piping, electrical power, and instrumentation wires pass through several split plugs on the west side of the cell. The process piping on the outside of the cell is contained within a glove bag, which provides a secondary containment as a precaution in case the process piping lines become contaminated. The vacuum pump, condenser, bubbler, GC, and the remainder of the instrumentation and valves are located inside this glove bag. Instrumentation and electrical power wires are routed through pass-through sleeves on the sides of the glove bag to the instrument rack and computer console.

Figure 2.1. Fuel Element Drying System Components (in-cell)

Figure 2.2. Fuel Element Drying System Components (ex-cell)

The instrument rack contains the readout/control units for the pressure sensors, moisture sensor, flow controllers, along with the heat trace temperature controllers, data acquisition/control unit, turbo pump controller, GC laptop computer, and uninterruptible power supplies. The computers for the DACS and MS are located next to the instrument rack. The following sections provide more detailed descriptions of the components for these subsystems.

2.2 Vacuum Pumping System

The vacuum pumping system provides the pressures and flows required for the proposed IPS processes. This system connects the furnace retort with all the other components of the test system through various valves, fittings, and piping. The vacuum pumping system consists of the following components:

- scroll pump for evacuating the system to pressures below 1 Torr
- water condenser with refrigerated chiller for gross removal of water
- valves and piping for connecting the various components and controlling the flow direction
- particulate filters to prevent spread of contamination
- heating cords with temperature controllers for preventing condensation in lines.

2.2.1 Varian Scroll Pump

The system vacuum pump is a Varian model 300DS scroll pump. This pump has an ultimate vacuum pressure less than 10^{-2} Torr and a peak pumping speed of 250 l/min (8.8 cfm). These pressures and flows are more than adequate for simulating the conditions of the proposed IPS vacuum processes. For a single fuel element, this amount of flow may be more than desired. Therefore, a metering valve was installed on the pump inlet to throttle the flow to lower levels as required. The desired system pressure is achieved by either using the metering valve or flowing ultra high purity (UHP) argon into the system through the entire gas loop or via a direct injection of ballast gas at the pump inlet. The use of argon gas helps to prevent the in-leakage of moisture-containing air through small system leaks (which are difficult to eliminate) that would interfere with process monitoring equipment.

2.2.2 Water Condenser

The scroll vacuum pump can be damaged by condensation of liquid water in the scroll mechanism, and, since each fuel element is wet at the start of each test, the possibility of pump damage was considered. A water condenser with corresponding chiller was installed in the system to condense the bulk of the water before it reaches the pump. This condenser can be valved into the system in series with the scroll vacuum pump or can be bypassed if not needed. The condenser cannot trap all the liberated free water, but is efficient at removing the majority of free water in the system. The condenser is only used

during the first phase of a Cold Vacuum Drying (CVD) test for a single fuel element. The condenser was custom fabricated specifically for this system. Detailed sketches and specifications for the condenser are given in Ritter et al. (1998).

2.2.3 Piping, Valves, and Filters

The vacuum pumping system connects the system components through various valves, fittings, and piping. A simplified piping schematic for the system is shown in Figure 2.3. This schematic shows the basic flow path of gases through the system that was used for this test, along with the relative locations of the major components, valves, and instruments. Detailed system piping diagrams are provided in Ritter et al. (1998), along with approximate lengths for the piping lines. As seen in Figure 2.3, there are numerous valves in the system that are used to direct the flow to and from the various components. Most of the valves in the system are ball valves and range from 1/4 in. to 1/2 in. nominal size. The system piping is constructed of thin wall tubing (1/4 in. to 1/2 in. OD) and is typically connected using simple Swagelok fittings (tees, elbows, unions, etc.). Ports for gas sampling/analysis and monitoring of system pressure, temperature, and humidity are also provided at key locations in the system piping. Special fittings and pipe-threaded fittings are used in some locations for connecting piping to the process instruments.

Particulate filters are installed in the system on both the inlet and outlet to the retort to help prevent the spread of contamination to the system piping on the outside of the hot cell. These filters are constructed of a microporous fiberglass media in a stainless steel housing. They are 99.9% efficient for particulates that are 0.2 microns and larger in size. Two different size filters, manufactured by Matheson, are used in the system.

2.2.4 System Line Heaters

All of the stainless steel tubing that carries gases into the furnace retort and resultant gases from the retort is heated to about 75°C to ensure condensable water vapor remains in the gas phase. Simple heat "cords" capable of being wrapped upon each other (as required at tees, elbows, and other connections) were found to be a good heating method for this system. The heating cords are controlled by simple proportional controllers. Type-K thermocouples are installed on each heated line to monitor and record temperature using the DACS.

2.3 Process Heating System

The whole element furnace is a 4-ft-long, resistively heated, clam-shell furnace. The furnace, a Series 3210 supplied by Applied Test Systems (ATS), has a temperature rating of 900°C and total heating capacity of 13,800 W. The internal dimensions are 5 in. ID by 45 in. long. The furnace has three separate sets of heating elements that allow the heating to be controlled in zones; each zone is 15 in. long and supplies up to 4600 W heating. The zones can be controlled separately to establish a flat temperature profile within the furnace, even though heat is lost preferentially out the end with the retort entry flange. A heat reflector consisting of several thin Inconel plates is used to reduce heat loss from the flange end of

Figure 2.3. Generalized View of Test System

the retort. The furnace controller is an ATS Series 3000, which consists of three programmable, self-tuning proportional with integral and derivative controllers. These controllers are also interfaced to the DACS, which is capable of providing limited input to the controllers as required.

The retort, an ATS Series 3910, is an Inconel tube fitted with a gas inlet tube at one end and a gasketed flange at the other. Of all high-temperature materials, Inconel series 600 was selected to reduce the amount of oxidation and water pickup by the retort and associated components. Experience has shown that stainless steel components were easily affected by corrosion, which could then affect test results. The body of the retort is fabricated from schedule 40 Inconel pipe (4.5 in. OD, 4.026 in. ID), and the inside length is about 44.5 in. Seven type-K thermocouples are installed equidistant along one side of the retort and extend into the retort interior approximately 1/8 in. These thermocouples are used to monitor the retort temperature so that if a reaction with the fuel element occurs (which would locally raise the retort temperature), this event can be correlated with the approximate location on the fuel.

An Inconel sample/transfer boat is used to load the fuel element into the furnace. The boat is fabricated from an 11-gauge (0.120-in.-thick) Inconel 601 sheet, which is formed into a flattened u-shape. The boat has a weir and a swivel handle on each end. The weirs are used to keep free water or particulates contained in the boat as required.

2.4 Gas Supply/Distribution System

The gas supply system and vacuum pumping system together are capable of controlling the fuel element environment to vacuum or moderate pressure conditions, and/or exposing the fuel element to a variety of gases or gas mixtures. The gas loop is typically operated as a single-pass system with no capability for recirculation. The gas supply system consists of gas bottles; mass flow controllers; piping; and valves for metering argon, air, or oxygen through the system. A bubbler is also available for adding water vapor to the process gas stream as required, but it was not used in these tests.

The gas supply system contains three Matheson mass flow controllers calibrated for argon, air, and oxygen. All gases are typically specified "ultra high purity" and are additionally filtered for water using molecular sieve columns. Argon is the principal inert gas used as it is more dense than air, provides reasonable thermal conductivity, and requires simpler handling procedures than lighter gases such as helium. The argon purge gas is introduced into the retort through FE-01, which is a Matheson model 8272-0422 oxygen controller, recalibrated for argon gas at 25°C using a NIST-traceable bubble flow meter. Air and oxygen are not currently used because any oxidative steps have been deleted from the current IPS for the SNF. The manufacturer's specifications for the controllers' flow rate ranges are 0 – 304 sccm argon, 0 – 1000 sccm air, and 0 – 10 sccm oxygen. If higher flow rates are desired, a new mass flow controller with a higher range could be procured and installed in the system.

2.5 Gas Analysis Instrumentation

2.5.1 Balzers Omnistar Mass Spectrometer

The Balzers Omnistar Mass Spectrometer is a compact, computer-controlled, quadrupole MS capable of scanning to 300 amu. The unit is capable of monitoring up to 64 components within a gas stream with a nominal detection limit of less than 1 ppm for most gases other than hydrogen. The MS was used to monitor hydrogen, nitrogen (for air in-leakage), krypton, xenon, and other elements during the test.

The MS was modified as a result of early system testing and calibration to improve the time response to small changes in hydrogen pressure. Prior to testing, the MS was calibrated for hydrogen using mixtures of hydrogen and helium, and hydrogen and argon gas. The residence time of each gas could be measured in the quadrupole chamber, and it was observed that the hydrogen decay time was approximately four times as long as helium. This was not unexpected as turbomolecular pumps have a lower pumping efficiency for very light gases. In standard practice this is acceptable, but for these tests, where determining hydrogen could be very important, steps were taken to improve the hydrogen decay time. The MS vacuum system was modified by adding a stainless steel flanged tee, a gate valve, and a room-temperature hydrogen getter downstream from the quadrupole. Under vacuum the gate valve can be opened, exposing the getter to the system to help scavenge hydrogen from the system following analysis. This modification reduced the residence time of hydrogen in the system substantially, and decreased the background level of hydrogen by about a factor of 2. The getter improved the system response to transient events that may result in the release of hydrogen.

A Granville-Phillips variable leak valve, series 203, was added to the gas sampling inlet of the MS in order to permit operation over a wide range of system pressures. Without the leak valve, system pressures above about 40 Torr produce too much flow through the MS capillary tube, which overwhelms the turbo pump used to pump down the MS vacuum chamber. Flow through the leak valve can be continuously varied from 0.4 l/s to 10^{-11} l/s, which allows the MS inlet pressure to be controlled to any pressure desired, even if the system pressure varies dramatically. The pressure on the low-pressure side of the leak valve is measured using a Cole-Parmer sensor (PE-07) and recorded by the DACS. The inlet head pressure is divided by the pressure used for the calibration, and this factor is applied to the test data for calculating actual gas concentrations. The MS was calibrated at ~30 Torr head pressure with a certified gas standard consisting of 1050 ppmv hydrogen in argon.

2.5.2 MTI M200 Gas Chromatograph

The MTI M200 Gas Chromatograph is a high-speed GC that is used to monitor the quantities of hydrogen and other light gases in the furnace testing system gas loop. This instrument is interfaced with a laptop computer to record data. The GC is designed to operate at near-atmospheric pressure; thus it may be configured in two different ways for measurement purposes. At system pressures near atmospheric, the GC is configured to sample directly from the gas loop ahead of the system vacuum pump. When the system is under vacuum, the GC is configured to sample from the exhaust side of the vacuum pump. The gas output from the pump is sufficiently compressed so that the GC can sample and analyze this gas. The GC inlet pressure is measured using a Cole-Parmer pressure sensor (PE-08) and recorded by the DACS.

No correction for the difference in the sample pressure and calibration pressure is applied, since both are ~760 Torr (1 atm). The GC was calibrated with a certified gas standard consisting of 114 ppmv hydrogen in synthetic air.

2.6 Process Instrumentation

The furnace testing system contains several process instruments for monitoring moisture content, pressure, and temperature. The key instruments are as follows:

- Panametrics moisture monitor
- MKS Baratron pressure transducers
- Cole-Parmer pressure transducers
- Type-K thermocouple.

2.6.1 Panametrics Moisture Monitor

The Panametrics moisture monitor model MMS35 uses a solid electrochemical probe (model M2L) that measures moisture by measuring the characteristic capacitance of the probe as a function of the moisture in the gas phase. The sensor has a nominal dew point range of -110°C to 20°C. Previous testing indicated that contamination by radioactive elements (e.g., cesium) causes the probe to lose calibration and results in moisture readings that drift with time. To prevent contamination of the probe tip, the probe is installed in the gas loop downstream of two glass particulate filters. Further, the probes are changed following each test and surveyed for radioactive contamination. If no contamination is found, and the data correlate well with the data obtained from the MS, the readings are accepted.

A calibration verification procedure can be performed using calibrated water "leak" tubes. These tubes can be placed inside the furnace and, when heated, will establish a known water vapor pressure in the system. However, this procedure is time intensive; approximately 2 weeks are required to calibrate one probe over the range of moisture likely to be encountered in these tests. This procedure is only used if the moisture monitor results vary widely from the MS data.

Output of the moisture monitor is in dew point in degrees Celsius. For comparison with other test data, these dew point values were converted to water vapor pressure in Torr using the water and ice vapor pressure data shown in Table 2.1. Interpolation of the data was accomplished using a 6th-order polynomial fit to the log of the vapor pressure (VP) versus temperature data. The resulting conversion expression is as follows:

Table 2.1. Water and Ice Vapor Pressure Data Versus Temperature

Dew Point (°C)	Vapor Pressure (VP)		
	(Pa) ^(a)	(Torr)	Log (Torr)
-80	5.5000E-02	4.136E-04	-3.3834
-75	1.2200E-01	9.174E-04	-3.0374
-70	2.6100E-01	1.963E-03	-2.7071
-65	5.4000E-01	4.061E-03	-2.3914
-60	1.0800E+00	8.122E-03	-2.0904
-55	2.0930E+00	1.574E-02	-1.8030
-50	3.9360E+00	2.960E-02	-1.5287
-45	7.2020E+00	5.416E-02	-1.2663
-40	1.2840E+01	9.656E-02	-1.0152
-35	2.2350E+01	1.681E-01	-0.7745
-30	3.8010E+01	2.858E-01	-0.5439
-25	6.3290E+01	4.759E-01	-0.3224
-20	1.0326E+02	7.765E-01	-0.1099
-15	1.6530E+02	1.243E+00	0.0945
-10	2.5990E+02	1.954E+00	0.2910
-5	4.0176E+02	3.021E+00	0.4802
0	6.1129E+02	4.597E+00	0.6625
10	1.2281E+03	9.235E+00	0.9655
(a) CRC Press. 1997. <i>Handbook of Chemistry & Physics</i> , 78 th edition.			

$$VP(\text{Torr}) = \log^{-1} (Ax^6 + Bx^5 + Cx^4 + Dx^3 + Ex^2 + Fx + G) \quad (2.1)$$

where x = the measured dew point (°C) and

$$A = -6.7260 \cdot 10^{-12}$$

$$B = -1.7250 \cdot 10^{-9}$$

$$C = -1.7089 \cdot 10^{-7}$$

$$D = -7.2618 \cdot 10^{-6}$$

$$E = -2.9668 \cdot 10^{-4}$$

$$F = 3.4414 \cdot 10^{-2}$$

$$G = 0.66043$$

2.6.2 MKS Baratron Pressure Transducers

Two MKS Baratron model 690 calibrated pressure transducers coupled with MKS model 270 signal conditioners are used as the primary measurement for the overall system pressure. As shown in Figure 2.3, PE-01 measures the system pressure downstream of the retort outlet, whereas PE-06 measures the system pressure at the retort inlet. PE-01 indicates pressure in the range of 0.1 Torr to 10,000 Torr. The pressure range of PE-06 is 0.01 Torr to 1000 Torr. PE-06 was installed after the first two fuel

element drying tests to provide more accurate measurements than PE-01 for low pressures. PE-06 is therefore considered the primary system pressure measurement. In addition, the 270 signal conditioner procured with PE-06 has a special capability to remotely zero the transducer, which provides more accurate pressure measurements below 1 Torr.

An auxiliary high vacuum turbo pump is used to evacuate the inlet to PE-06 to well below 10^{-4} Torr, so that the transducer can be accurately re-zeroed. The 270 signal conditioner used with PE-01 does not have a remote zeroing. Both signal conditioners have analog outputs that are interfaced to the DACS so that system pressure is continuously recorded.

2.6.3 Cole-Parmer Pressure Transducers

Two Cole-Parmer model H-68801-53 diaphragm-type, calibrated pressure transducers are installed on the MS and GC sample lines, as indicated by PE-07 and PE-08 in Figure 2.3. These pressure measurements are used to normalize the MS and GC data so that actual gas concentrations in the system can be calculated from the relative concentrations measured. These sensors have a range of 0 to 1500 Torr with a resolution of 0.1 Torr, and an accuracy of $\pm 1\%$ or ± 1 Torr, whichever is larger. Both readout units (model H-68801-03) have analog outputs that are interfaced to the DACS so that these pressures are continuously recorded.

2.6.4 Thermocouples

Thermocouples provide a simple, reliable method for measuring system temperatures. As shown in Figure 2.3, over 20 thermocouples are installed at various locations in the system to provide key temperature measurements. The retort temperatures are of primary importance, and these temperatures are measured by thermocouples TE-04 through TE-10, which are positioned equidistant along the length of the retort. Other key temperature measurements include the retort center temperature (TE-20, which is a 30-in.-long thermocouple installed through the outlet end of the retort), retort inlet temperature (TE-21), condenser gas temperature (TE-19), and the condenser coolant temperature (TE-22). Thermocouples TE-11 through TE-17 are used for controlling the temperature of the heated lines. All thermocouple readings are continuously recorded using the DACS.

2.7 Data Acquisition and Control System

The DACS monitors system parameters, and controls the furnace and safety argon system. The DACS consists of a Hewlett Packard (HP) 3497A data acquisition/control unit, and an IBM-compatible computer. A National Instruments general purpose interface bus card, installed in the IBM-compatible computer, is used to communicate with the HP 3497A. The computer communicates with the furnace temperature controllers over serial port 0 using an RS-232/RS-485 converter. The DACS uses National Instruments LabView for Windows as the control software.

The DACS is designed to measure critical system parameters during fuel conditioning tests, including temperatures, pressures, flow rates, and moisture level. The measured parameters are converted to engineering units, displayed on the computer screen, and stored to disk at user-defined intervals. The data

files are stored in a tab-delimited format to allow importing into a standard spreadsheet or plotting program. A plotting screen also allows for plotting of up to six parameters at a time.

Limited control of the furnace can be performed with the DACS. Each of the three furnace zone temperatures can be remotely set by the DACS. In addition, the DACS allows the operator to start and stop the furnace and select one of four temperature profiles that are pre-programmed in the furnace temperature controllers. Note that these profiles must be programmed manually in the furnace controllers before using the DACS to select them.

3.0 Vacuum Drying Testing of Element 0309M

The drying test was performed in accordance with the requirements of *Test Plan for Whole Element Furnace Run 3*, SNFCT98:008:R00, and the individual Test Procedure, *Furnace Testing of N-Reactor Fuel Element 0309M*, PTL-004, Revision 0. These documents are located in the PNNL permanent project records for this test.

The testing consisted of three parts (discussed in this section):

- removing the fuel from its shipping canister, performing a visual inspection, loading the fuel onto the furnace system sample boat, and transferring it to the PTL G-Cell for loading into the furnace.
- drying the fuel element using a combination of Cold Vacuum Drying (CVD) and Hot Vacuum Drying (HVD) processes.
- unloading the furnace, performing a post-test visual inspection, and returning the fuel element to its shipping canister.

3.1 Fuel Element Transfer and Loading

3.1.1 Pre-Test Visual Inspection

The pre-test visual inspection was conducted using a high-resolution black and white video camera located outside the PTL F-Cell, where the sample unloading from the shipping canister and visual inspection were conducted. The results were recorded using a Panasonic Super-VHS resolution video recorder. This examination was conducted to document the condition of the fuel element prior to the test and to determine if any changes had occurred since it was removed from the K-West Basin and shipped to the PTL. The results of this inspection are presented in Section 4.1.

3.1.2 Fuel Element Rinsing

Fuel element 0309M had been stored in the PTL water storage pool contained in a single fuel element canister (SFEC) that was filled with K-Basin water. Prior to the start of the drying, the element was rinsed in F-Cell. This rinsing was accomplished by raising and lowering the element several times in the SFEC using one of the cell's manipulators.

A sample of material coating the fuel element was taken at this time. Following rinsing, the element was transferred to G-Cell for loading into the test retort.

3.2 Fuel Element Drying

The fuel element was subjected to cold and hot vacuum drying. The drying test was conducted in six phases:

1. Cold Vacuum Drying
2. Pressure Rise Tests
3. Hot Vacuum Drying (first step)
4. Hot Vacuum Drying (second step)
5. Hot Vacuum Drying (third step)
6. Post-Test Pressure Rise Test.

The nominal design conditions for each of these test phases are summarized in Table 3.1. Actual conditions for each phase are discussed below.

3.2.1 Cold Vacuum Drying

While the fuel element was being handled and prepared for the drying test, it was kept damp by sprinkling it with deionized water. The amount of surplus liquid water, though small, could not be ascertained. The element was then loaded into the furnace and the test started.

The furnace temperature was increased to approximately 50°C and allowed to stabilize. The system vacuum pump was then turned on, and the system water condenser valved in. When the system pressure dropped to a reasonable level, the vacuum pump was valved out and only the condenser left in the system. When the system pressure became lower than the condenser could extract, the condenser was valved out of the gas loop, and the vacuum pump valved back in. This process was repeated until the vacuum pump could safely evacuate the remaining water. No argon was injected during CVD in this test. CVD was conducted for approximately 0.7 hr at retort pressures ranging from ~30 Torr down to ~1 Torr. The purpose of the CVD portion of the test was to determine if CVD is successful in removing the majority of the free water from the system in a reasonable length of time.

3.2.2 Pressure Rise Tests

The Pressure Rise Tests involved isolating the system from the effects of flowing gas, and continued vacuum pumping and measuring any system pressure increases while at CVD pressure and temperature conditions. The purpose of the Pressure Rise Test was to determine the effectiveness of the preceding CVD process. This test was conducted by valving the vacuum pump out of the gas loop, turning off the argon gas flow, and closing the exhaust valves in the gas loop. The condition for acceptance of this portion of the test is a total system pressure rise of less than 0.6 Torr in a 1-hr time period. If this condition is not met, the system is re-opened to the vacuum pump and the Pressure Rise Test repeated. Two pressure rise sequences were necessary to meet the 0.6 Torr/hr pressure rise requirement, covering a total time period of ~2 hr.

Table 3.1. Summary of Nominal Test Design Conditions

Test Segment	Nominal Test Condition^(a)
A. Cold Vacuum Drying System Configuration Test Temperature, °C Atmosphere Pressure, Torr Gas Flow Rate, cc/min Gas Species Monitored Duration, hr	Pump on, no argon flow 50 Vacuum <5 0 H ₂ , H ₂ O, N ₂ , O ₂ , CO ₂ , Ar, Kr, Xe CVD will be conducted until the total pressure in the retort falls below 0.5 Torr.
B. Pressure Rise Test System Configuration Test Temperature, °C Atmosphere Initial Pressure, Torr Gas Flow Rate, cc/min Gas Species Monitored Pressure Rise (acceptable levels, Torr) Duration, hour	Test Chamber Isolated 50 Vacuum <5 0 H ₂ , H ₂ O, N ₂ , O ₂ , CO ₂ , Ar, Kr, Xe <0.6 1
C. Hot Vacuum Drying (Step 1) System Configuration Test Temperature Range, °C Atmosphere Pressure, Torr Gas Flow Rate, cc/min Gas Species Monitored Duration, hr	Pump on, argon gas flow 75 Vacuum, Ar background 15 300 H ₂ , H ₂ O, N ₂ , O ₂ , CO ₂ , Ar, Kr, Xe ~17
D. Hot Vacuum Drying (Step 2, heatup) System Configuration Test Temperature Range, °C Temperature Ramp Rate, °C/hr Atmosphere Pressure, Torr Gas Flow Rate, cc/min Gas Species Monitored Duration, hr	Pump on, argon gas flow 75 to 400 10 Vacuum, Ar background 15 300 H ₂ , H ₂ O, N ₂ , O ₂ , CO ₂ , Ar, Kr, Xe ~34

Table 3.1. (contd)

Test Segment	Nominal Test Condition ^(a)
E. Hot Vacuum Drying (Step 3)	
System Configuration	Pump on, argon gas flow
Test Temperature, °C	400
Atmosphere	Vacuum, Ar background
Pressure, Torr	<5
Gas Flow Rate, cc/min	300
Gas Species Monitored	H ₂ , H ₂ O, N ₂ , O ₂ , CO ₂ , Ar, Kr, Xe
Duration, hr	~8
F. Pressure Rise Test	
System Configuration	Test Chamber Isolated
Test Temperature, °C	50
Atmosphere	Vacuum
Initial Pressure, Torr	<5
Gas Flow Rate, cc/min	0
Gas Species Monitored	H ₂ , H ₂ O, N ₂ , O ₂ , CO ₂ , Ar, Kr, Xe
Duration, hr	1
(a) Nominal test design conditions. Actual values are given in the text.	

3.2.3 Hot Vacuum Drying, Step 1

Following completion of the Pressure Rise Tests, the vacuum pump was re-opened to the system retort, argon gas flow was established at a rate of 324 cc/min, and the retort temperature was raised to ~80°C. This condition was held for a period of ~17 hr at a retort pressure of ~15 Torr. This portion of the test can be used to obtain isothermal hydrogen and water release data for assessing oxidation of the fuel at low temperatures.

3.2.4 Hot Vacuum Drying, Step 2

The second step of the HVD process involved raising the temperature of the retort from ~80°C to ~400°C at a carefully controlled rate while maintaining the same argon flow and pressure conditions. Thus, any release of gas species during this temperature rise can be assigned to a specific temperature. The second step of HVD was conducted for about 34 hr.

During this step, hydrogen may be released from the fuel through the decomposition of uranium hydride (Cotton 1988); this reaction is rapid at temperatures greater than 250°C:

Water may also be liberated by various hydrated species found on fuel elements, such as hydrates of uranium oxides, aluminum hydroxides, and hydrated iron oxides. The released water can also react with the fuel element to generate hydrogen through the reactions:

3.2.5 Hot Vacuum Drying, Step 3

The final step of the HVD process involved holding the temperature of the retort at $\sim 400^\circ\text{C}$ while again maintaining the same argon flow and pressure conditions as in steps 1 and 2. This step will yield isothermal release data for any remaining hydrated species on the fuel element, and for oxidation of uranium by any remaining water. This final step of the HVD process was conducted for about 8 hr.

3.2.6 System Cooldown and Post-Test Pressure Rise Test

Following completion of the final HVD step, the system retort was allowed to cool to $\sim 50^\circ\text{C}$, at which time another Pressure Rise Test was conducted to determine the baseline in-leakage rate of air into the retort from the cell environment. Knowing this rate is important to allow for correction of the system and moisture pressure increase rates determined in the initial post-CVD Pressure Rise Test(s). Since the conditions for the post-HVD are identical to those used for the initial test(s), the assumption is made that the air in-leakage rate should be nearly the same as well.

3.3 Calculation of Water and Hydrogen Inventories

Assuming ideal gas behavior of the water vapor, total water inventory (g) in the system during those portions of the test conducted with argon flowing into the retort can be approximated from the measured water vapor pressure and the argon gas flow as follows:

$$\frac{dm}{dt} = \frac{M}{V_0} \cdot \frac{P_w}{(P_t - P_w)} \cdot \frac{dV}{dt} \quad (3.4)$$

where dm/dt is the rate of water removal in grams per minute, M is the molecular mass of water in grams per mole, dV/dt is the flow rate in liters per minute (at the calibration temperature of 25°C), V_0 is the molar volume of gas at 25°C and 1 atmosphere in liters per mole, P_w is the partial pressure of water vapor in Torr, and P_t is the total pressure in Torr. The total amount of water released is given by integrating the rate data over time.

The hydrogen inventory may be calculated in a similar fashion with the $[P_w/(P_t - P_w)]$ expression in the above equation replaced with the measured atom fraction of hydrogen (ppmv/ 10^6). Hydrogen

concentration in ppmv is output from both the GC and MS. For the purpose of this report, all hydrogen data are plotted in Torr-l rather than grams. At the calibration conditions of the argon flow controller, 1 Torr-l is equivalent to approximately 0.11 mg of hydrogen.

The assumptions made in estimating the water and hydrogen values are:

- The flow into the retort is approximately equal to the flow out (i.e., contributions to the flow from other gas species such as hydrogen are neglected).
- The argon mass flow is referenced to 25°C (as determined from the calibration of the flow gauges).
- The sample gas is at the same temperature as the calibration gas (GC and MS measurements).

4.0 Visual Examinations of Element 0309M

An N-Reactor fuel assembly consists of an inner element and outer element made from a uranium alloy co-extruded with a Zircaloy-2 cladding. Both elements are annular, right-cylinders. The inner element has a smaller outer diameter and is held in place within the outer element.

Fuel element 0309M, chosen for Run 3, was an outer element removed from the K-West Basin in 1996. The element had been in sealed water storage in the K-West Basin since 1983. This fuel element was selected to represent a classification of fuel damage termed "broken in half" (Lawrence 1997). The furnace drying test series (this is test run 3 of 8) were intended to progress from intact (unbreached) fuel elements to severely damaged fuel elements. This fuel element is the first damaged or broken fuel element tested that had an exposed metallic uranium surface. It was only about 3/5 of the complete outer element; the other portion of the element has been kept in water storage at the PTL basin. The fuel element did not appear to have experienced extensive corrosion, and thus was a good choice for use in the early stages of the testing series.

The fuel element had been kept in K-Basin water at the PTL storage basin since it was loaded into its SFEC and shipped to the facility in 1996. The first relatively detailed examination of the fuel element was conducted just before the drying test and is discussed below.

4.1 Pre-Test Visual Examination

The fuel element appeared to have a "translucent" coating on the cladding surface. Figure 4.1 shows a view of the intact end of the fuel element. Light-colored regions on the side of the fuel element are indicative of a coating separating from the cladding surface. The coating layer appears to cover the entire surface of the fuel element.

Figure 4.2 shows a portion of a side view of the element while the surface was scraped with a putty knife. The white-circled region highlights an area where the putty knife scratched through a non-adherent section of the coating. The coating fractured in a brittle manner, leaving small chips on the surface. These chips were collected for phase analysis by X-ray diffraction (XRD), which will be conducted at a later date. Some samples may be mounted for examination by scanning electron microscope (SEM) to measure the thickness of these chips and determine the amount of material present on the surface. No other attempt was made to determine the coating thickness during the visual examinations.

The broken surface of the end section of the fuel element is shown in Figure 4.3. The surface appears to show little or no additional evidence of corrosion or other physical degradation. Furthermore, the damaged end appears to have changed little since the fuel element was selected for testing in 1996 (though this is a qualitative judgment). The exposed fuel surface was scratched with a putty knife and small, dark-colored particulates could be scratched off. To prevent risk of changing the overall surface

Coating layer partially separated from the fuel cladding surface

Figure 4.1. Pre-Test View of Intact End of Fuel Element 0309M

Figure 4.2. Pre-Test View of Side Section of Fuel Element 0309M
with Putty Knife Used for Scraping

Figure 4.3. Pre-Test View of Damaged End of Fuel Element 0309M

condition, the scratching was limited to a very small area. There were too few particulates scratched off the surface to warrant collection for analysis. The fuel cladding did appear to extend slightly (~0.5 to 1 mm) beyond the surface of the exposed uranium fuel material. It could not be determined from the visual examination if the coating covered the damaged material.

4.2 Post-Test Visual Examination

A post-test visual examination was conducted using a small color video camera placed in G-Cell. Figure 4.4 is a still image captured from the videotape showing the intact end of the fuel element following the test. The most striking observation was the transformation of the fuel coating from a translucent, semi-adherent coating to a white substance that had mostly peeled from the cladding surface in wafer-like chips. Samples of these post-test chips were collected for phase analyses by XRD. These analyses could not be completed in time to include in this report. It has been speculated that the coating was a hydrated aluminum oxide material that dehydrated to aluminum oxide during the drying test. However, the chemical reaction that transformed the coating will not be determined until the XRD analyses are completed.

The fuel element did not appear to undergo any other significant changes. A crack in the damaged end of the fuel element that was found in the post-test visual examination (Figure 4.5) was not observed in the pre-test examination. This crack was visible simply because it was filled with coating material that turned a white color during the drying test. The coating material was partly adhered in some places on the fuel element. A small band of material was present along the inside of the element and in scattered locations along the outer surface (Figure 4.6). The material was easily scraped off using a putty knife and would likely have fallen off with continued handling in the hot cell.

Figure 4.4. Post-Test View of Intact End of Fuel Element 0309M with Residual Coating

Figure 4.5. Post-Test View of Damaged End of Fuel Element 0309M

Figure 4.6. Post-Test View of Side Section of Fuel Element 0309M

5.0 Experimental Results

In the following sections, the experimental data collected during the drying test are expanded and plotted for each segment. Summary results from the test are plotted in Figure 5.1. This figure shows the system moisture level response to the pressure changes and the retort tube temperatures during the test. Time intervals for the various test segments are shown in the upper section of the plot, and also outlined in Table 5.1. The temperatures shown in Figure 5.1 were recorded from one of seven thermocouples (TE-07) on the system located near the center of the retort. The pressure is from the 0 to 1000 Torr Baratron sensor (PE-06) located upstream of the retort.

5.1 Cold Vacuum Drying

The water release from the CVD portion of the test is shown in Figure 5.2. This plot spans the period when the furnace was loaded with the SNF element through to the Pressure Rise Test. The baseline moisture partial pressure in the system prior to heating was ~10 Torr at a retort temperature of ~21°C. Total system pressure was 737 Torr, with no argon gas flow. After heating to ~50°C, the moisture pressure and system pressure stabilized at ~7 Torr and 830 Torr, respectively. Based on the pressure differences at these two temperatures, and assuming ideal gas behavior, there is an approximately 20 Torr pressure difference. This pressure difference has been observed in all the previous tests, except for the first dry-run, and may have been due to gases evolved during the heatup, such as hydrogen from moisture reactions, and gases dissolved in the free water. Another explanation for the calculated pressure difference is that the average retort temperature was somewhat greater than 50°C.

The CVD commenced at an elapsed time (ET) of 323 min when the vacuum pump was opened briefly in order to "rough-out" the system retort to ~30 Torr (total pressure). Figure 5.2 shows that the moisture pressure initially rose, reaching a maximum of about 12 Torr after several minutes, then dropping slowly to ~5 Torr over the next 25 min. At ~351 min ET, the moisture pressure began to drop sharply, reaching a final value of ~0.3 Torr at the end of CVD. The sudden drop in moisture pressure coincides with the time at which the system condenser was valved out of the system and the retort re-opened to the vacuum pump. Approximately 5 ml of water were observed in the condenser during CVD. Because of the design of the condenser, however, the observed water is likely to be an underestimation of the total water collected.

5.2 Pressure Rise Tests

The results of the two pressure rise phases of the drying test (post-CVD and post-HVD) are shown in Figures 5.3 and 5.4. The purpose of the post-HVD test was to determine the ambient air in-leakage rate into the system as it had been configured for the drying test. While under vacuum conditions, with no argon flow, any air in-leakage will contribute to the data signals observed for the various process gases measured during the test, particularly water and hydrogen. As discussed above, the data plotted for the total pressure is from the 0 to 1000 Torr Baratron sensor (PE-06) located upstream of the retort. This sensor has higher sensitivity and lower noise than the 0 to 10,000 Torr Baratron located downstream of

Figure 5.1. Drying of SNF Element 0309M, Summary Plot

Table 5.1. Fuel Element 0309M Drying Run Time Line

Activity	Date/Time	Elapsed Time (min)
Start of Test		
Heat furnace to ~50°C	12/7/97 10:58	142
Cold Vacuum Drying Test		
Open pump valve and condenser to furnace	12/7/97 13:59	323
Close pump valve	12/7/97 14:05	329
Open pump valve, close condenser valve	12/7/97 14:28	352
Pressure Rise Test(s)		
Close pump (isolate furnace)	12/7/97 14:43	367
Open pump valve	12/7/97 15:28	412
Close pump (isolate furnace)	12/7/97 15:36	420
Open pump valve	12/7/97 16:38	482
Hot Vacuum Drying Test (Step 1)		
Start argon flow (~324 cc/min)		
Raise furnace temperature to ~80°C and hold	12/7/97 16:39	483
Hot Vacuum Drying Test (Step 2)		
Raise furnace temperature to ~400°C @ 10°C/min	12/8/97 9:25	1488
Hot Vacuum Drying Test (Step 3)		
Hold furnace temperature at ~400°C	12/9/97 19:29	3533
System Cooldown		
Reduce temperature of retort to ~50°C, maintain argon flow	12/10/97 3:44	4028
Post-Test Pressure Rise Test		
Turn off argon flow		
Close pump valve (isolate furnace)	12/11/97 8:47	5771
Turn off furnace heaters, end test	12/11/97 9:54	5838

the retort and is, therefore, more accurate in determining small pressure rise rates. For calculation of total water mass removed from the retort, under conditions of argon gas flow, pressure data from the 0 to 10,000 Torr sensor (PE-01) were used, as this sensor is closer to the moisture sensor. Differences in the pressure indications of the two sensors are small, however, and therefore negligible when compared with overall system uncertainties.

The post-CVD Pressure Rise Test was conducted over an ET of 367 min to 483 min, and was conducted in two steps in order to meet the pressure rise criterion of 0.6 Torr/hr. In the first step, the total pressure and the moisture pressure showed an initial non-linear region followed by a longer linear region. A regression fit to the linear region (dotted lines in the figure) yielded a total pressure rise rate of ~0.71 Torr/hr, just above the 0.6 Torr/hr criterion. The rate of water vapor pressure increase in the linear region was ~0.28 Torr/hr. As noted in Section 3.2.2, the test procedure calls for a second Pressure Rise Test in the event of a failure. Since the first test nearly met the 0.6 Torr/hr criterion, the system was evacuated to below 0.5 Torr, and a second post-CVD Pressure Rise Test was conducted.

The results of the second pressure rise step are also shown in Figure 5.3, and show similar trends to the first step. Here, regression fits to the linear portions of the data indicate pressure rise rates of

Figure 5.2. Drying of SNF Element 0309M, Cold Vacuum Drying

Figure 5.3. Drying of SNF Element 0309M, Post-CVD Pressure Rise Test

Figure 5.4. Drying of SNF Element 0309M, Post-HVD Pressure Rise Test

~0.44 Torr/hr for total pressure and ~0.14 Torr/hr for moisture pressure. The difference between the total pressure rise rates and the moisture pressure rise rates for the two steps is ~0.43 Torr/hr and ~0.32 Torr/hr, respectively.

Assuming that the water vapor pressure increase is from water sources within the test system, and assuming ideal gas behavior of the water vapor, the rate of desorption of the water will be constant, given by:

$$\frac{dn}{dt} = \frac{V}{RT} \cdot \frac{dP}{dt} \quad (5.1)$$

where n is the number of moles of gas, V is the volume of the system (~10,000 cm³), R is the gas constant (82.06 cm³·atm/g·mol·K), T is the temperature (~326 K), and dP/dt is the rate of change in the pressure given by the slope of the regression line. The total amount of water released to the system during the Pressure Rise Tests is given by the integral of the above equation over the two tests. Assuming an average moisture release rate of 0.21 Torr/hr and a total period of 115 min, the total amount of water released was ~4 mg. Using a total surface area of ~7800 cm² for the system (total surface area of the retort, sample boat, tubing, and ~1/2 outer fuel element), and 10¹⁵ atoms per cm² as the monolayer gas density on surfaces, ~17 monolayer equivalents of H₂O were evaporated.

The results of the post-HVD pressure rise measurements are shown in Figure 5.4. Again, both the total pressure and the moisture pressure show an essentially linear increase with time, however, with significantly lower slopes than observed for the earlier post-CVD measurements. The total pressure rise has a regression slope of ~0.11 Torr/hr, and the moisture pressure rise has a slope of ~0.00041 Torr/hr. The ratio of the water pressure rise to the total pressure rise is ~0.004, which is similar to that expected assuming the observed moisture pressure rise was from humidity in air in-leakage from the cell environment (air at 20°C and 25% relative humidity would yield a water pressure to total pressure ratio of ~0.007).

Comparison of the total and moisture pressure rises from the post-CVD and post-HVD Pressure Rise Tests indicates that the source of the total pressure rises observed in the initial post-CVD tests was only partially from residual moisture. Additionally, the differences between the total pressure rises and the moisture pressure rises for the post-CVD tests are significantly higher than can be explained by air in-leakage into the retort as measured in the post-HVD test. This suggests that other sources of gas are responsible for most of the observed total pressure rise in the post-CVD tests.

5.3 Hot Vacuum Drying

The first segment of the HVD, shown in Figure 5.5, includes the ramp and hold from ~50°C to ~80°C in flowing argon gas (324 cc/min) under partial vacuum. HVD-1 was run over an ET of 483 min to 1488 min. The moisture pressure decreased steadily from ~50 mTorr to ~1 mTorr during the ~80°C period. Total system pressure was essentially constant over the first HVD phase at ~14 Torr. Total water removed during HVD-1 was ~94 mg.

Figure 5.5. Drying of SNF Element 0309M, Hot Vacuum Drying - Step 1

Figure 5.6. Drying of SNF Element 0309M, Hot Vacuum Drying – Step 2

The second HVD phase involved maintaining the same system conditions as in HVD-1 but raising the temperature from $\sim 80^{\circ}\text{C}$ to $\sim 400^{\circ}\text{C}$ at a rate of 10°C/hr . HVD-2 was run over an ET of 1488 min to 3533 min. Total system pressure varied over a range of ~ 13 to ~ 14 Torr. As shown in Figure 5.6, upon initiation of this second phase, the moisture partial pressure increased significantly, reaching a maximum value of ~ 400 mTorr before dropping asymptotically to a value of ~ 12 mTorr at $\sim 400^{\circ}\text{C}$. Three distinct peaks are evident in the moisture release, at temperatures of $\sim 130^{\circ}\text{C}$, $\sim 187^{\circ}\text{C}$, and $\sim 222^{\circ}\text{C}$. These moisture peaks are an indication of water release from chemisorbed sites (i.e., hydrated species) at higher temperatures. Total water removed during the second phase of HVD was ~ 1.7 g, approximately 18 times that removed during the first phase of HVD.

The final phase of HVD is shown in the left-hand side of Figure 5.7 (ET of 3533 min to 4028 min), and covered the temperature hold period at $\sim 400^{\circ}\text{C}$. This period is characterized by a steady decrease in the moisture pressure from ~ 12 mTorr to ~ 4 mTorr.

Following the final HVD phase, the system was allowed to cool to $\sim 50^{\circ}\text{C}$ in preparation for the post-test Pressure Rise Test (discussed above). Water removed during the system cooldown was ~ 20 mg.

5.4 Gas Chromatograph Measurements

The GC is calibrated to measure hydrogen in the sample gas. As discussed earlier, the hydrogen concentration is converted from ppmv to Torr-l so that the absolute quantity of hydrogen gas released can be determined independent of argon flow rate. At the calibration conditions for the argon flow gauge (~ 760 Torr and $\sim 25^{\circ}\text{C}$), 1 Torr-l of hydrogen is equivalent to 0.11 mg. The GC yielded data for the release of hydrogen in the gas stream during the HVD steps and for part of the cooldown. During these parts of the test, argon was flowing through the system at a rate of about 324 cc/min. It was not possible to sample with the GC during the CVD portion of the test since it was conducted with no flow of argon gas.

Measured hydrogen release during the HVD segments of the drying test are shown in Figure 5.8. As is evident, there are two major peaks and several smaller ones. The major peaks occurred at temperatures of $\sim 220^{\circ}\text{C}$ (~ 0.21 Torr-l/min) and $\sim 265^{\circ}\text{C}$ (~ 0.31 Torr-l/min). Two smaller peaks occurred at $\sim 187^{\circ}\text{C}$ (~ 0.06 Torr-l/min) and $\sim 300^{\circ}\text{C}$ (~ 0.16 Torr-l/min). The 220°C peak correlates with a large water release at the same time, and is likely due to uranium oxidation by water. The 270°C peak is likely due to the decomposition of uranium hydride. The broad peak that is unresolved from the 270°C peak occurring at $\sim 300^{\circ}\text{C}$ is likely due to oxidation of uranium or uranium hydride by water. A small rise in the hydrogen release is also evident at a temperature close to 400°C ; however, it is not clear whether this is a "peak," as it occurred at the end of the temperature ramp cycle. This peak also corresponds to a small rise in the water data.

Figure 5.9 shows the deconvolution of the hydrogen data. The quantity of hydrogen measured during HVD-2 that is attributable to the decomposition of uranium hydride is approximately 47 Torr-l (5 mg). This quantity is equivalent to ~ 0.5 g of UH_3 . The quantity of hydrogen released corresponding to the

Figure 5.7. Drying of SNF Element 0309M, Hot Vacuum Drying - Step 3

Figure 5.8. Drying of SNF Element 0309M, Hydrogen Release During HVD

Figure 5.9. Deconvolution of Hydrogen Peaks During HVD-2

water release at 220°C is ~45 Torr-l (4.8 mg). The water released during this period (ET 2000 – 2500 min) is approximately 1.3 g. This equates to a 3.3 mole% conversion, assuming that all the hydrogen measured during this period is the result of oxidation of uranium by water. Based on the deconvolution of the GC hydrogen data, the remainder of the hydrogen, which is released at temperatures between ~300°C and ~400°C is approximately 70 Torr-l (7.6 mg), with the majority released at ~300°C. Approximately 0.19 g of water was released at temperatures between ~300°C and ~400°C. This equates to a 36 mole% conversion, assuming that all the hydrogen released was the result of the high-temperature oxidation of fuel by water. It is likely that the hydrogen released at these higher temperatures is a combination of oxidation of fuel by water and further hydride decomposition.

Both the water and the hydrogen signals decreased as the system temperature stabilized at ~400°C, with the rate of hydrogen release decreasing from ~0.05 Torr-l/min to ~0.02 Torr-l/min. This suggests that the source of the hydrogen was oxidation of uranium by water. During cooldown, the rate of hydrogen release drops even more rapidly. A possible explanation is that small quantities of uranium hydride (relative to the uranium) in the fuel are stabilized by the metal and therefore difficult to decompose. Uranium hydride with a small deficiency in hydrogen has been shown to have greater stability than the stoichiometric hydride (Cotton 1988). It is unlikely that hydrogen-deficient uranium hydride is present in the fuel, but it is possible that some UH_3 gradient region may exist near the broken end. A more likely mechanism, however, is that the remaining water in the system is oxidizing the fuel at temperatures greater than 300°C. This mechanism is supported by the good correlation of the hydrogen and water signals at temperatures greater than 300°C.

Two "spikes" are evident in the GC data at ET ~2680 and ~3000, one positive and one negative. These peaks are observed on both GC columns but at somewhat different times. The cause of the spikes is not yet clear. Since they are not present in the MS hydrogen data, they are regarded as "noise transients" and are not interpreted as hydrogen release or gettering events.

The total quantity of hydrogen released during HVD was ~180 Torr-l (~19 mg), attributable mainly to decomposition of uranium hydride and reaction of water released from oxy-hydrides with uranium metal.

5.5 Mass Spectrometer Measurements

The Balzers Omnistar MS was used to collect hydrogen and other gas release data over the test run. Hydrogen data from the MS are also shown in Figure 5.8. As is evident, the two larger peaks observed on the MS data are also present on the GC data and are well correlated. The magnitude of the MS hydrogen peaks, however, is smaller. One possible explanation for this is as follows. The MS was calibrated for hydrogen at an inlet pressure of ~30 Torr. During the drying test, the actual inlet pressure was measured by the Cole-Parmer diaphragm gauge (PE-07), and these data were then used to normalize the hydrogen data from the MS. However, inlet pressures during the test ranged from only about 2 to 3 Torr, which were at the low end of the pressure range for the Cole-Parmer gauge, suggesting possible inaccuracies in the MS normalizations. Two modifications are planned to resolve this issue: 1) replacement of the MS inlet pressure gauge with one that is more accurate in this low pressure range, and 2) re-calibration of the MS at lower inlet pressures. These modifications will allow for more accurate normalization of the MS to actual sampling pressures.

No significant krypton or xenon releases were noted in the MS data. Small xenon and krypton peaks were observed in the data; however, they were well correlated with nitrogen, indicating an atmospheric origin.

6.0 Discussion

Approximately 5 ml of water were observed in the condenser during the condenser pumpdown phase of CVD. The criterion used for judging the completion of the CVD step is a system pressure of 0.5. Using this criterion, the post-CVD Pressure Rise Test did not meet the criterion of <0.6 Torr/hr and, therefore, a second test was conducted. This second test passed the pressure rise criterion. Approximately 4 mg of water were removed during both Pressure Rise Tests. Comparison of the pressure rises from the post-CVD and post-HVD tests indicates that the source of the total pressure rises observed in the post-CVD tests is only partially from residual moisture, suggesting that other sources of gas are responsible for most of the observed total pressure rise. As the temperature was only $\sim 50^{\circ}\text{C}$, it is unlikely that metal oxy-hydrate decomposition was a significant source of this water. Therefore, this release can likely be interpreted as coming from *free* water that was trapped under the observed coating and not completely released during CVD. An estimate of the amount of free water remaining after CVD can be made from the change in the water removal rate during the CVD period extrapolated to a longer time; however, since the CVD period was so short it would be difficult to obtain a meaningful prediction from the data.

During the first segment of HVD, approximately 94 mg of water were removed at temperatures below 80°C . The second phase of HVD released approximately 1.7 g of water with peaks at $\sim 130^{\circ}\text{C}$, 187°C , and 222°C , the latter being the largest. The final phase of HVD at 400°C released approximately 63 mg of water. An additional 20 mg of water were released during cooldown. This indicates that the fuel element still contained small residual quantities of water even after the drying test was completed.

The water released after the post-CVD Pressure Rise Tests is attributed chiefly to the release of water from metal oxy-hydrates. The evidence for this is the distinct release peaks at specific temperatures. The bulk of the water removal occurred during the second phase of the HVD, which entailed the temperature ramp from $\sim 80^{\circ}\text{C}$ to $\sim 400^{\circ}\text{C}$. The fact that distinct peaks were evident in the moisture release indicates water release from chemisorbed sites (i.e., hydrated species) at higher temperatures. Thermal decomposition of the hydrated species was significant in controlling the removal of water from the system during the HVD. Water was still being released at a reasonable rate at the end of the 400°C HVD-3 step, indicating some quantity of water remaining in the system. As a result, a temperature above 400°C may be required for complete drying of the hydrated species within a reasonable period of time.

Hydrogen data were obtained from the GC during HVD when argon was flowing through the system. Hydrogen was observed starting at about 150°C and continued to evolve at increasing rates with temperature to a maximum level of ~ 0.21 Torr-l/min at 222°C and then dropping and rising again to a maximum level of ~ 0.3 Torr-l/min at 270°C . The second release corresponds to the decomposition of uranium hydride, the first to oxidation of the fuel by water. At 410°C , the level of hydrogen began to decrease with time. Total hydrogen release during HVD was ~ 180 Torr-l (~ 19 mg). It can also be noted that no significant krypton or xenon release events were observed in the MS data that correlated with the observed hydrogen releases.

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Reports are written separately for the whole element drying test series as follows:

System Design Description for the Whole Element Furnace Testing System

Spent Fuel Drying System Test Results (First Dry-Run)

Spent Fuel Drying System Test Results (Second Dry-Run)

Spent Fuel Drying System Test Results (Third Dry-Run)

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Drying Results of K-Basin Fuel Element 3128W (Run 2)

Drying Results of K-Basin Fuel Element 0309M (Run 3)

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