Pacific Northwest National Laboratory

Operated by Battelle for the
U.S. Department of Energy

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

J. Abrefah
G. S. Klinger
B. M. Oliver
T. A. Flament

S. C. Marschman
P. J. MacFarlan
G. A. Ritter

RECEIVED
OCT 13 1998
OSTI

July 1998

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY

operated by

BATTELLE

for the

UNITED STATES DEPARTMENT OF ENERGY

under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401.

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

This document was printed on recycled paper.

(9/97)

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

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

J. Abrefah
G. S. Klinger
B. M. Oliver
T. A. Flament^(a)

S. C. Marshman
P. J. MacFarlan
G. A. Ritter

July 1998

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Richland, Washington 99352

(a) Numatec Hanford Corporation.

Summary

An N-Reactor outer fuel element that had been stored underwater in the Hanford 100 Area K-East 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 N-Reactor 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 an open K-East canister (3128W) during the first fuel selection campaign conducted in 1995, and has remained in wet storage in the Postirradiation Testing Laboratory (PTL, 327 Building) since that time. Although it was judged to be breached during in-basin (i.e., K-Basin) examination, visual inspection of this fuel element in the hot cell indicated that it was likely intact. Some scratches on the coating covering the cladding were identified before the furnace test.

The drying test was conducted in the Whole Element Furnace Testing System located in G-Cell within the PTL. This test system is composed of three basic systems: the in-cell furnace equipment, the system gas loop, and the analytical instrument package. Element 3128W was subjected to the 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 55°C under vacuum for about 68 hr
- Pressure Rise Test under static low-pressure conditions at 55°C for 4 hr
- Gas Evolution Test at 78°C, at near-atmospheric pressure, using an argon background gas for approximately 25 hr
- Hot Vacuum Drying (HVD) at about 310°C under vacuum for a total of 141 hr (24 hr for heatup to 310°C at atmospheric pressure, followed by 117 hr at 310°C in vacuum)
- Water Removal Verification at 400°C under vacuum for 5 hr
- System cooldown to ambient conditions.

Results of the Pressure Rise and Gas Evolution Tests suggest that most of the free water in the system was released during the extended CVD cycle (68 hr versus 8 hr for the first run). An additional ~0.34 g of water was released during the subsequent HVD phase, characterized by multiple water release peaks, with a principal peak at ~180°C. This additional water is attributed to decomposition of a uranium

hydrate ($\text{UO}_4 \cdot 4\text{H}_2\text{O} / \text{UO}_4 \cdot 2\text{H}_2\text{O}$) coating that was observed to be covering the surface of the fuel element to a thickness of $\sim 1.6 \text{ mg/cm}^2$. A limited quantity of hydrogen ($\sim 9 \text{ mg}$) was also released during HVD, mainly at temperatures above 300°C , likely from hydride decomposition.

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 Radioactive Waste Management *Quality Assurance Requirements and Description (QARD)*. Compliance with the QARD is mandatory for projects that 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 N-Reactor Element 3128W*.

Contents

Summary.....	iii
Quality Assurance.....	v
Acronyms.....	xiii
1.0 Introduction.....	1.1
2.0 Whole Element Furnace Testing System	2.1
2.1 Major Systems Overview.....	2.1
2.2 Vacuum Pumping System.....	2.4
2.2.1 Varian Scroll Pump.....	2.4
2.2.2 Water Condenser.....	2.4
2.2.3 Piping, Valves, and Filters	2.5
2.2.4 System Line Heaters	2.5
2.3 Process Heating System.....	2.5
2.4 Gas Supply/Distribution System.....	2.7
2.5 Gas Analysis Instrumentation	2.8
2.5.1 Balzers Omnistar Mass Spectrometer	2.8
2.5.2 MTI M200 Gas Chromatograph	2.8
2.6 Process Instrumentation	2.9
2.6.1 Panametrics Moisture Monitor.....	2.9
2.6.2 MKS Baratron Pressure Transducers.....	2.10
2.6.3 Cole-Parmer Pressure Transducers	2.10
2.6.4 Thermocouples.....	2.11

2.7	Data Acquisition and Control System.....	2.11
3.0	Vacuum Drying Testing of Element 3128W.....	3.1
3.1	Fuel Element Transfer and Loading	3.1
3.1.1	Pre-Test Visual Inspection.....	3.1
3.1.2	Fuel Element Rinsing.....	3.1
3.2	Fuel Element Drying.....	3.1
3.2.1	Cold Vacuum Drying	3.3
3.2.2	Pressure Rise Test	3.4
3.2.3	Gas Evolution Test.....	3.4
3.2.4	Hot Vacuum Drying, Step 1.....	3.4
3.2.5	Hot Vacuum Drying, Step 2.....	3.4
3.2.6	Water Removal Verification	3.4
3.3	Post-Test Visual Examination.....	3.5
3.4	Calculation of Water and Hydrogen Inventories	3.5
4.0	Visual Examinations of Element 3128W	4.1
4.1	Pre-Test Visual Examination	4.1
4.2	Post-Test Visual Examination.....	4.1
5.0	Experimental Results.....	5.1
5.1	Cold Vacuum Drying.....	5.1
5.2	Pressure Rise Test	5.3
5.3	Gas Evolution Test.....	5.6
5.4	Hot Vacuum Drying.....	5.6
5.5	Water Removal Verification	5.9

5.6 Gas Chromatograph Measurements	5.9
5.7 Mass Spectrometer Measurements	5.15
6.0 Discussion	6.1
7.0 References	7.1
8.0 Supporting Documents and Related Reports.....	8.1

Figures

2.1	Fuel Element Furnace Components (in-cell)	2.2
2.2	Fuel Element Furnace Components (ex-cell).....	2.3
2.3	Generalized View of the Furnace Testing System	2.6
4.1	End View of N-Reactor Fuel Element 3128W.....	4.2
4.2	Side View of N-Reactor Fuel Element 3128W	4.2
4.3	Post Test Visual Examination of Element 3128W.....	4.3
4.4	Brushing of Element 3128W Following Drying Test	4.4
5.1	Drying of Element 3128W, Summary Plot.....	5.2
5.2	Drying of Element 3128W, Cold Vacuum Drying	5.4
5.3	Drying of Element 3128W, Pressure Rise Test.....	5.5
5.4	Drying of Element 3128W, Gas Evolution Test	5.7
5.5	Drying of Element 3128W, Hot Vacuum Drying (Step 1)	5.8
5.6	Drying of Element 3128W, Hot Vacuum Drying (Step 2)	5.10
5.7	Drying of Element 3128W, Water Removal Verification.....	5.11
5.8	Hydrogen Release During Gas Evolution	5.12
5.9	Hydrogen Release During Hot Vacuum Drying - Step 1.....	5.13
5.10	Hydrogen Release During Hot Vacuum Drying - Step 2.....	5.14

Tables

2.1	Water and Ice Vapor Pressure Data Versus Temperature.....	2.10
3.1	Summary of Test Conditions	3.2
5.1	Fuel Element 3128W Drying Test Time Line.....	5.3
6.1	Summary of Water Released During the Drying Test Cycles	6.1

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 for 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
XRD	X-ray diffraction
VP	vapor pressure

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 basin 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 fuel elements 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 second of those tests, which was conducted on an N-Reactor outer fuel element removed from K-East canister 3128W. This fuel element (referred to as Element 3128W) 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 testing was conducted in the Whole Element Furnace Testing system, described in Section 2.0, located in the Postirradiation Testing Laboratory (PTL, 327 Building). The test conditions and methodology are given in Section 3.0. Section 4.0 describes the results of visual examinations, and Section 5.0 provides the experimental results. These results are further discussed in Section 6.0.

(a) Operated by Battelle for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

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 an 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

Figure 2.1. Fuel Element Furnace Components (in-cell)

Figure 2.2. Fuel Element Furnace Components (in-cell)

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.

The instrument rack contains the readout/control units for the pressure sensors, moisture sensor, and 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, and type-K thermocouples are installed on each heated line so the DACS can be used to monitor and record temperature.

2.3 Process Heating System

The whole element furnace is a 4-ft-long, resistively heated, clam-shell furnace. The furnace, 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

Figure 2.3. Generalized View of the Furnace Testing System

profile within the furnace even though heat is lost preferentially out the end with retort entry flange. A heat reflector consisting of several thin Inconel plates is used to reduce heat loss from the flange end of 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. The recalibration resulted in a flow rate range of 0 - 324 sccm argon. 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 air and oxygen controllers' flow rate ranges are 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 was measured (but not recorded by the DACS) using a Cole-Parmer sensor (PE-07). 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 that the GC can sample and analyze this gas. 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 thermocouples.

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:

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

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

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

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

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

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

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

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

$$G = 0.66043$$

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. *Handbook of Chemistry & Physics*, 78th edition.

2.6.2 MKS Baratron Pressure Transducers

An MKS Baratron model 690 calibrated pressure transducer (PE-01), coupled with an MKS model 270 signal conditioner, was used as the primary measurement for the overall system pressure. The signal conditioner has an analog output that is interfaced to the DACS so that system pressure may be continuously recorded. This unit measures pressure in the range of 0.1 Torr to 10,000 Torr, and is located downstream of the retort outlet. [A lower range Baratron (0.01 Torr to 1000 Torr) was added after the first two fuel element drying tests to provide more accurate low-pressure measurements.]

2.6.3 Cole-Parmer Pressure Transducers

A Cole-Parmer model H-68801-53 diaphragm-type, calibrated pressure transducer is installed on the MS line as indicated by PE-07 in Figure 2.3. These pressure measurements were intended for normalization of the MS data so that actual gas concentrations in the system could be calculated from the relative concentrations measured. This sensor has 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. The readout unit (model H-68801-03) has an analog output that is interfaced to the DACS so that this pressure may be 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 the 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 3128W

The test was performed in accordance with the requirements of *Test Plan for Whole Element Furnace Runs 1, 2, and 3*, SNFCT97:053:R00 and the individual Test Procedure, *Furnace Testing of N-Reactor Fuel Element 3128W*, PTL-170 Revision 0. These documents are located in the PNNL permanent project records for this test.

The entire test 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 Panasonic Super-VHS video camera located outside the PTL F-Cell (adjacent to G-Cell), where the sample was unloaded from the shipping canister. 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 1996 when the fuel element was first brought to the PTL. The results of this inspection are presented in Section 4.1.

3.1.2 Fuel Element Rinsing

Fuel element 3128W had been stored in the PTL water storage pool contained in a single fuel element canister (SFEC) that was filled with K-Basin water. Before the start of the drying test, the element was rinsed in F-Cell. This rinsing involved raising and lowering the element several times in the SFEC using one of the cell's manipulators. 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 Test
3. Gas Evolution Test
4. Hot Vacuum Drying (first step)
5. Hot Vacuum Drying (second step)
6. Water Removal Verification.

The conditions used for these test phases are summarized in Table 3.1. Each test phase is described below.

Table 3.1. Summary of Test Conditions

Test Segment	Test Conditions for Element 3128W
A. Cold Vacuum Drying System Configuration Test Temperature, °C Atmosphere Pressure, Torr Gas Flow Rate, cc/min Gas Species Monitored Duration, hr	Normal ~55 Vacuum, Ar background 9 ~55 H ₂ , H ₂ O, N ₂ , O ₂ , CO ₂ , Ar, Kr, Xe The duration for CVD was at least 2 hr or until free water being removed read either background or below detectable limits.
B. Pressure Rise Test System Configuration Test Temperature, °C Atmosphere Initial Pressure, Torr Gas Species Monitored Pressure Rise (acceptable levels, Torr) Duration, hr	Test Chamber Isolated ~55 Vacuum, Ar background 9 H ₂ , H ₂ O, N ₂ , O ₂ , CO ₂ , Ar, Kr, Xe <3 4
C. Gas Evolution Test System Configuration Test Temperature, °C Atmosphere Initial Pressure, Torr Gas Species Monitored Pressure Rise (acceptable levels, Torr) Duration, hr	Test Chamber Isolated ~78 Argon 760 (~atmospheric) H ₂ , H ₂ O, N ₂ , O ₂ , CO ₂ , Ar, Kr, Xe <120 25

Table 3.1. (contd)

Test Segment	Test Conditions for Element 3128W
D. Hot Vacuum Drying (Step 1, heatup)	
System Configuration	Normal
Test Temperature Range, °C	~75 to 310
Temperature Ramp Rate, °C/hr	10
Atmosphere	Argon
Pressure, Torr	760 (~atmospheric)
Gas Flow Rate, cc/min	323
Gas Species Monitored	H ₂ , H ₂ O, N ₂ , O ₂ , CO ₂ , Ar, Kr, Xe
Duration, hr	24
E. Hot Vacuum Drying (Step 2, drying)	
System Configuration	Normal
Test Temperature, °C	312
Atmosphere	Vacuum, Ar background
Pressure, Torr	17
Gas Species Monitored	H ₂ , H ₂ O, N ₂ , O ₂ , CO ₂ , Ar, Kr, Xe
Duration, hr	117
F. Water Removal Verification	
System Configuration	Normal
Test Temperature, °C	400
Atmosphere	Vacuum, Ar background
Gas Species Monitored	H ₂ , H ₂ O, N ₂ , O ₂ , CO ₂ , Ar, Kr, Xe
Duration, hr	5

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. There were no pools of water in the sample boat; however, droplets did exist. The element was then loaded into the furnace, and the test started.

The furnace temperature was raised to about 50°C and allowed to stabilize. The system vacuum pump was then turned on, and the system water condenser valved in. Once the system pressure reached the vapor pressure of free water, the vacuum pump was valved out of the gas loop, and the condenser valved in to remove the majority of the free water from the system. During this time, the pressure steadily dropped until the water vapor pressure became lower than the condenser could extract. At this point, the water content in the gas phase began to rise, and the condenser was valved out of the system while the vacuum pump was valved back in to continue evacuating the system.

The vacuum pump is capable of reducing the system pressure to levels lower than desired for CVD. To stabilize the system pressure near the desired value of about 5 Torr, dry, UHP argon was metered into

the system. CVD was conducted at about 9.2 Torr for about 67 hr. The flow of UHP argon (about 55 cc/min) through the furnace system also minimized in-leakage of cell air into the retort tube.

3.2.2 Pressure Rise Test

The Pressure Rise Test involved isolating the fuel element from the effects of flowing gas, and continued vacuum pumping and measuring any system pressure increases while at CVD pressure and temperature conditions. 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. This test was conducted over a 4-hr period.

3.2.3 Gas Evolution Test

The Gas Evolution Test was conducted at 78°C in a background of UHP argon gas at nearly 1 atm total system pressure. This test was performed by raising the system pressure and temperature simultaneously to the test conditions. The system pressure was elevated by metering UHP argon gas into the system until the desired pressure was reached. The gas flow was then turned off, and the fuel element isolated for 25 hr at these conditions.

3.2.4 Hot Vacuum Drying, Step 1

The first step of HVD involved heating the fuel element from 78°C to 310°C at a slow ramp rate of 10°C/hr in a flowing argon atmosphere near 1 atm system pressure. UHP argon was allowed to flow through the system at about ~324 cc/min and exhausted to the hot cell. This portion of the test took about 24 hr.

3.2.5 Hot Vacuum Drying, Step 2

The second part of the HVD test cycle required the system to be evacuated while the temperature was held at 310°C. Again, argon gas was metered into the system to establish the vacuum conditions in the test system. The second step of the HVD process was conducted for about 117 hr.

3.2.6 Water Removal Verification

Previous studies (Abrefah et al. 1998a) have shown that water may be released from the fuel through the decomposition of uranium oxy-hydrates. Thus, to check for the presence of high-temperature hydrates and evaluate the completeness of the CVD and HVD cycles, the element was heated to 400°C. The test was conducted under vacuum with argon metered into the system as the background gas. The test was conducted over a period of about 5 hr.

3.3 Post-Test Visual Examination

The removal of the element from the furnace test system was documented using a Philips digital color camera. The entire outer surface of the element was inspected using this camera, and the results recorded using a Super-VHS videotape recorder (See Section 4.2).

3.4 Calculation of Water and Hydrogen Inventories

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

$$\frac{dm}{dt} = \frac{M}{V_0} \cdot \frac{P_w}{(P_t - P_w)} \cdot \frac{dV}{dt} \quad (3.1)$$

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 the 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. For the purposes 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.
- The argon mass flow is referenced to 25°C.
- The sample gas is at the same temperature as the calibration gas (GC and MS measurements).

4.0 Visual Examinations of Element 3128W

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 outside diameter and is held in place within the outer element to form the assembly.

Fuel element 3128W, chosen for Run 2, was an outer element removed from the K-East Basin in 1996. The element had been placed in the basin sometime between 1973 and 1987. Fuel stored in the K-East Basin is in open canisters (not sealed as in the K-West Basin). The in-basin visual inspection performed at the time of selection did not indicate that the element was breached, and there was no apparent damage from reactor discharge, handling, or storage.

The fuel element had been kept in K-Basin water at the PTL storage basin since it was loaded into an SFEC and shipped to the facility in 1996. The fuel element was removed from its storage container in late 1996 for detailed examination and subsequently returned to the PTL basin storage (Pitner 1997). Again, the fuel element did not appear to have any visible breaches.

4.1 Pre-Test Visual Examination

Before the drying test, the fuel element was removed from the SFEC and examined using a high-resolution black and white video camera. Two still images captured from the video are shown in Figures 4.1 and 4.2. Figure 4.1 shows one of the intact ends of the fuel element. The visual examination suggested that no additional corrosion or damage had occurred on/to the fuel element since the 1996 in-basin examination. Both ends of the fuel element were intact, and no apparent breaches were observed on the surfaces of the fuel element. The visual inspection did reveal that at least one spot-welded "shoe" was broken from the element, but the weld areas also appeared intact.

Figure 4.2 shows a portion of a side view of the element. The visual inspection identified the presence of large areas covered by surface coatings, light gray to white in color, which were scratched in several locations. Where the coating was scratched, the cladding surface appeared to be visible. A sample of the coating material was collected for characterization by X-ray diffraction (XRD) to be conducted at a later date. However, if this coating is related to the coating materials removed from other fuel elements (Abrefah et al. 1998b), it is likely a mixture of uranium oxy-hydrates.

4.2 Post-Test Visual Examination

The post-test visual examination was conducted using a small color video camera placed in the PTL G-Cell. Figure 4.3 is a still image captured from the videotape, showing the entire fuel element, following the test. The element appeared to be intact following the test, with no breaches or other observed defects.

Figure 4.1. End View of N-Reactor Fuel Element 3128W

Figure 4.2. Side View of N-Reactor Fuel Element 3128W

Figure 4.3. Post-Test Visual Examination of Element 3128W. As-fabricated N-Reactor outer element (Mark IVE) has the dimensions: 66.3 cm length; 6.15 cm OD; 4.31 cm ID.

The surface coating did undergo an observable change as a result of the drying process. The coating color changed from light gray to a dirty orange. The coating was still easily scraped, and a sample was collected for XRD analysis at a later date. The orange color of the post-test coating may be an indication that oxy-hydrates are converted to UO_3 , which will be further examined during the XRD analysis. No attempt was made to quantify the thickness of the coating, as the material was only present in a thin layer and scraped away in places due to handling and testing. The right end of the fuel element (Figure 4.3) probably sat at the bottom of the fuel canister in a sludge layer, protecting it from developing the layer of coating material.

Following the test, portions of the fuel element were scraped and brushed to retrieve samples of the altered surface coating. Figure 4.4 shows a captured video image of the brushing activities. A small abrasive pad was used to scrub the fuel cladding surface as had been done in previous examinations (Abrefah et al. 1998b). Although the coating was easily removed by brushing, little loose material was observed in the fuel element sample boat following the test, which suggests the coating was reasonably adherent. The collected sample will be analyzed by XRD at a later date.

Figure 4.4. Brushing of Element 3128W Following Drying Test

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 temperature 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.

5.1 Cold Vacuum Drying

The water released during the CVD portion of the test is shown in Figure 5.2. The baseline moisture partial pressure in the system prior to heating was ~3 Torr. This moisture pressure was below the theoretical saturation pressure at this temperature for the argon/air gas mixture (residual air from when the fuel element was loaded) at ~16°C. This saturation pressure is ~14 Torr, yielding a relative humidity of about 26% in the system. The moisture pressure decreased from the baseline to ~2 Torr when the system was heated to ~55°C. The reason for this small decrease is not completely understood, but could be from hygroscopic fuel element material remaining from the first drying test (Run 1).

The total pressure of the closed system increased from 756 Torr to 867 Torr when the temperature was increased at the start of the test from 16°C to 53°C. Theoretically, for an ideal gas the expected pressure rise due to a temperature increase from 16°C to 53°C is 97 Torr, approximately 14 Torr below the measured pressure rise. This may be due to gases evolved during the heatup to 50°C, 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.

Figure 5.2 also shows that the moisture pressure reached a maximum of about 14 Torr. The temperature plot in Figure 5.2 indicates the retort tube, and most probably the fuel element, had not reached the 50°C nominal temperature before the system was evacuated. Evacuating the system with the water condenser and scroll pump resulted in a decrease in the total pressure as well as in the partial pressure of moisture. The decrease in the total pressure was more rapid than the decrease in the moisture pressure. The slight system pressure increase shown as a step in Figure 5.2 was due to the introduction of argon gas into the system to provide a controlled background atmosphere (~55 cc/min of UHP argon). Also, after about 1800 min, a small variation of the retort temperature had a very slight influence on the water release.

The water signal was continuing to decrease even after a CVD cycle of ~4000 min. The water signal measured by the humidity probe (~1 mTorr) was equivalent to the value measured for the first intact element (Run 1) after ~1300 min. For the entire CVD cycle, the total quantity of water released was ~0.25 g.

Figure 5.1. Drying of Element 3128W, Summary Plot

Table 5.1. Fuel Element 3128W Drying Test Time Line

Activity	Date/Time	Elapsed Time (min)
Start of Test		
Heat furnace to ~53°C	10/24/97 09:31	0
Cold Vacuum Drying Test		
Open pump valve and condenser to furnace	10/24/97 13:19	228
Close pump valve		
Open pump valve, close condenser valve		
Start Ar flow to attain a retort pressure of ~5 Torr	10/24/97 14:23	292
Pressure Rise Test		
Close pump and Ar flow valves (isolate furnace)	10/27/97 8:57	4285
Gas Evolution Test		
Raise furnace temperature to ~75°C and	10/27/97 12:59	4527
Start Ar flow at ~300 cc/min		
Stop Ar flow when furnace pressure reaches ~1 atm (~760 Torr)	10/27/97 13:29	4558
Hot Vacuum Drying Test (Step 1)		
Raise furnace temperature to ~300°C @ 10°C/min		
Start Ar flow at ~300 cc/min (vent to cell)	10/28/97 14:11	6040
Hot Vacuum Drying Test (Step 2)		
Hold furnace temperature and Ar flow rate		
Open pump valve	10/29/97 14:30	7499
Water Removal Verification		
Raise furnace temperature to ~400°C	11/03/97 11:20	14509
Turn off furnace heaters, end test	11/03/97 16:10	14799

5.2 Pressure Rise Test

The Pressure Rise Test results are shown in Figure 5.3. Noise on the total pressure data is due to undersampling of the Baratron pressure gauge output and resolution limitations with the 0 to 10,000 Torr Baratron sensor. A second Baratron sensor (0 to 1000 Torr), with increased data sampling, was incorporated into the system for subsequent fuel element runs.

As is evident in Figure 5.3, the total pressure rise is approximately linear, with a regression slope of ~0.029 Torr/hr. The moisture pressure rise is also linear with a slope of ~0.59 mTorr/hr. This value is about four times lower than the value obtained during the first run. The contribution of the moisture pressure rise to the total pressure rise is ~2%. If the moisture had been coming solely from humidity (assuming 25% relative humidity at 20°C) in the cell air from in-leakage, the moisture contribution would have been only ~0.6%. The higher moisture contribution suggests additional sources of water from the

Figure 5.2. Drying of Element 3128W, Cold Vacuum Drying

Figure 5.3. Drying of Element 3128W, Pressure Rise Test

element and/or retort. The linearity of this release, and the small quantity of moisture evolved, is consistent with the partial evaporation of a surface film. Since the slope of the line did not change for the duration of the test, this suggests that the surface moisture was not reduced to less than a monolayer.

Assuming ideal gas behavior of the water vapor, the rate of desorption of the water will be constant, given by:

$$\frac{dn}{dt} = \frac{kV}{RT} \quad (5.1)$$

where n is the number of moles of gas, V is the volume of the system ($\sim 9000 \text{ cm}^3$), R is the gas constant ($82.06 \text{ cm}^3 \cdot \text{atm/g-mol} \cdot \text{K}$), T is the temperature (326 K), and k is a constant and equal to the slope of the regression line (i.e., dP/dt). The total amount of water released to the system during the Pressure Rise Test is given by the integral of the above equation. For a period of 4 hr, the total amount of water released was $\sim 20 \text{ } \mu\text{g}$.

5.3 Gas Evolution Test

Figure 5.4 shows the increase in moisture partial pressure during the Gas Evolution Test at a furnace temperature of about 78°C . The release of moisture occurred over four distinct regions. The first region showed negligible rise in the moisture pressure. This may be due to the slow response of the fuel element to the retort temperature ramp. This first region was followed by a rapid linear increase in the water vapor pressure, likely from delayed heating of the element. The third region of pressure rise was also linear with a slightly smaller slope than the preceding region. This latter region likely corresponds to the point at which the fuel element temperature reached a constant temperature.

The rate of pressure rise in this equilibrium region was 1.1 mTorr/hr . This rate is higher than that determined at 50°C , suggesting a temperature-activated desorption process for the water release.

The total amount of water released during the Gas Evolution Test can be estimated using the final water partial pressure ($\sim 60 \text{ mTorr}$) and the total volume of the system ($\sim 9000 \text{ cm}^3$), $\sim 0.45 \text{ mg}$.

5.4 Hot Vacuum Drying

The HVD segment of the test, shown in Figure 5.5, includes the ramp from 78°C to 310°C in flowing argon gas (324 cc/min) at atmospheric pressure. The moisture pressure decreased from $\sim 110 \text{ mTorr}$ to $\sim 65 \text{ mTorr}$ when the gas flow was established in the system. This decrease in water pressure was followed by a complex water release curve with one major peak and smaller ones before and after. The major peak (1.68 Torr) was observed at $\sim 162^\circ\text{C}$. The water vapor pressure at the end of the first step of the HVD cycle was $\sim 220 \text{ mTorr}$. With the same methodology as described above for the CVD cycle, the total amount of water released during the first phase of HVD was $\sim 0.21 \text{ g}$.

Figure 5.4. Drying of Element 3128W, Gas Evolution Test

Figure 5.5. Drying of Element 3128W, Hot Vacuum Drying (Step 1)

Figure 5.6 shows the continuation of the HVD test segment. Clearly, removing moisture from the system by the vacuum pump is more efficient than only flowing gas through the system. The moisture pressure decreased sharply from ~220 mTorr to ~0.1 mTorr at the end of the HVD-2 cycle. The HVD was conducted at a temperature near 310°C. The total amount of water release during the second phase of HVD was ~0.13 g.

The data from the HVD (especially the first cycle) suggest slow release kinetics of the moisture indicative of decomposition from chemically bound water. The slow decrease of the moisture level suggests that the water removal process is kinetically controlled by thermal decomposition of the hydrated species.

5.5 Water Removal Verification

This segment of the test was conducted to determine if there was any moisture remaining in the system following the HVD. Figure 5.7 shows the moisture response to the final temperature ramp to 400°C. As is evident in the figure, the water pressure is seen to increase about 20 min after the temperature increase from 310°C began. The quantity of water released during the water removal test was small, at ~2.4 mg.

5.6 Gas Chromatograph Measurements

The GC is calibrated to measure hydrogen in the sample gas, and yielded data for the release of hydrogen in the gas stream during the CVD and HVD phases of the test. During these phases, argon was flowing through the system at a rate of ~55 cc/min (CVD) and ~324 cc/min (HVD), respectively. It was not possible to sample for hydrogen using the GC during the Gas Evolution Test since it was conducted with no flow of argon gas. Additionally, there were significant gaps in the GC data collection due to problems with the data acquisition system. These gaps included the time periods 383 min to 4273 min, 4568 min to 6020 min, 6205 min to 7284 min, and 11582 min to 14484 min.

Figure 5.8 shows the hydrogen concentration as a function of time in the gas stream, together with plots of temperature and moisture partial pressure during the initial phase of CVD at ~50°C. The moisture level in the gas stream varied from ~14 Torr to ~0.1 Torr during CVD. Collection of hydrogen data commenced at an elapsed time (ET) of 292 min with a noticeable peak to a value of ~0.08 Torr-l/min, followed by a rapid decline to an equilibrium value of ~0.007 Torr-l/min, suggesting some low level of hydrogen release during the remainder of CVD. The hydrogen peak coincided with the initiation of argon flow at ~55 cc/min. Total hydrogen release during the peak was ~0.9 Torr-l (~0.1 mg).

Figures 5.9 and 5.10 show two hydrogen peaks observed during the HVD phase of the test at ~300°C. As was the case during CVD, both peaks were associated with changing system conditions, the first (~0.35 Torr-l/min) occurring at the end of the gas release test (argon at ~1 atm to vacuum), and the second

Figure 5.6. Drying of Element 3128W, Hot Vacuum Drying (Step 2)

Figure 5.7. Drying of Element 3128W, Water Removal Verification

Figure 5.8. Hydrogen Release During Gas Evolution

Figure 5.9. Hydrogen Release During Hot Vacuum Drying - Step 1

Figure 5.10. Hydrogen Release During Hot Vacuum Drying - Step 2

(~0.31 Torr-l/min) occurring at the transition from HVD-1 to HVD-2 (argon flow at ~1 atm to argon flow at vacuum). Total hydrogen release estimates for the two peaks are ~12 Torr-l (~1.2 mg) and ~46 Torr-l (~5 mg), respectively.

5.7 Mass Spectrometer Measurements

The Balzers Omnistar MS was used to collect hydrogen and other gas release data over the test run. For periods of time when the furnace system was at atmospheric pressure, however, the MS variable leak valve had to be used because the inlet pressure to the MS was too high to allow operation of the system to sample the gas directly. Additionally, the pressurization of the system after CVD, and subsequent depressurization after HVD-1, complicated the data analysis of the MS signals. As a result, meaningful concentration data were not obtained from the MS for the release of hydrogen or fission gases.

Nonetheless, a segment of the MS hydrogen data collected during HVD is shown in Figure 5.10 for comparison with the GC data. As is evident, the broad peak in the GC data at the initiation of the HVD-2 step (~7600 min ET) corresponds to a similar peak in the MS data at the same time. Krypton and xenon releases were also observed in the MS data, which roughly corresponded to this hydrogen release. The much larger "peak" in the MS data at ~7750 min does not correspond to any peak in the GC data and is, therefore, considered to be anomalous.

6.0 Discussion

Water released from the fuel element may be classified into two general categories: released as free water and released by decomposition of hydrated species. The quantities of water measured during each of the test segments are listed in Table 6.1. Generally, the water detected by the moisture monitor at temperatures of 75°C and below was due to release of free (i.e., not chemically bound) water in the system, and any water release observed above 75°C was due to thermal decomposition of hydrated species.

Most of the free water was released during the CVD cycle that lasted about 68 hr. The small quantities of water observed during the Pressure Rise Test following the CVD cycle and the Gas Evolution Test suggest that complete removal of the free water was not achieved. The presence of hydrated species on the fuel element could affect the results of both the Pressure Rise and Gas Evolution Tests.

The water release curve above 75°C is characteristic of the release of chemically bound water for some hydrated species. This is evidenced by:

- the observation of a surface coating on the fuel element noted during the pre-test visual examination, which may be uranium peroxide hydrate (Abrefah et al. 1998b)
- the change in color of that coating after the test (from gray/white to dirty orange)
- the apparent decomposition of the coating over a temperature range of 75°C and 310°C with a maximum release rate at about 180°C
- the slow decrease in the water partial pressure during the 50°C CVD cycle, suggesting decomposition of the coating.

The moisture release above 75°C is attributed to decomposition of hydrated species that existed in the coating material and is characterized by multiple water release peaks. The multiple peaks may be due to either a multi-step decomposition process of a single hydrated species, or the decomposition of different

Table 6.1. Summary of Water Released During the Drying Test Cycles

Test Segment	Temperature Range (°C)	Amount of Water (mg)
Cold Vacuum Drying	55	250
Pressure Rise Test	55	0.02
Gas Evolution	78	0.45
Hot Vacuum Drying, Step 1	78 - 310	210
Hot Vacuum Drying, Step 2	310	130
Water Removal Verification	310 - 400	2.4

hydrate forms. The most significant moisture release occurred at a temperature of $\sim 180^{\circ}\text{C}$. Although the coating material has not been analyzed using XRD, based upon the change in color and previous observations and analyses of K-East fuel elements (Abrefah et al. 1998b), it may be reasonable to assume the surface coating is composed of $\text{UO}_4 \cdot 4\text{H}_2\text{O}$ or $\text{UO}_4 \cdot 2\text{H}_2\text{O}$. This is also supported by the observation of a peak in the water release data at a temperature of 160°C , which is typical of the decomposition of these hydrated species. In that case, the water release above 75°C might be attributed to the decomposition of $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ to UO_3 . The quantity of water ($0.45 + 210 + 130 + 2.4 = 343$ mg) equates to 3220 mg of $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ on the fuel element (about 1.6 mg/cm^2). These values are similar to those documented in Abrefah et al. (1998b) for several K-East fuel element samples.

From the data available from the GC, hydrogen release by the fuel element was small (~ 9 mg). The maximum hydrogen release was observed at $\sim 300^{\circ}\text{C}$. There are two sources for the observed hydrogen: 1) hydrogen from the reaction of released moisture with uranium, and 2) hydrogen from decomposition of uranium hydride inclusions in the fuel matrix. During this run, most of the water was removed at higher temperatures; consequently, some of the hydrogen observed at temperatures $>75^{\circ}\text{C}$ can be ascribed to uranium hydride decomposition. It is also possible that pinhole breaches in the cladding, followed by subsequent corrosion of the fuel, generated small quantities of uranium hydride. However, at temperatures $<75^{\circ}\text{C}$, where water was retained, the hydrogen may be associated with uranium/moisture reactions, with a small contribution from water reaction with the furnace system.

7.0 References

Abrefah, J., H. C. Buchanan, and S. C. Marschman. 1998a. *Drying Behavior of K-East Canister Sludge*. PNNL-11628, Pacific Northwest National Laboratory, Richland, Washington.

Abrefah, J., S. C. Marschman, and E. D. Jenson. 1998b. *Examination of the Surface Coatings Removed from K-East Basin Fuel Elements*. PNNL-11806, Pacific Northwest National Laboratory, Richland, Washington.

Pitner, A. L. 1997. *Visual Examinations of K East Fuel Elements*. HNF-SD-SNF-TI-045, DE&S Hanford, Inc., Richland, Washington.

Ritter, G. A., S. C. Marschman, P. J. MacFarlan, and D. A. King. 1998. *Whole Element Furnace Testing System*. PNNL-11807, Pacific Northwest National Laboratory, Richland, Washington.

Westinghouse Hanford Company (WHC). 1995. *Hanford Spent Nuclear Fuel Project Integrated Process Strategy for K Basins Spent Nuclear Fuel*. WHC-SD-SNF-SP-005, Rev. 0, Richland, Washington.

8.0 Supporting Documents and Related Reports

Abrefah, J., and S. C. Marschman. 1997. *Test Plan for Whole Element Furnace Runs 1, 2, and 3*. SNFCT97:053:R00, Pacific Northwest National Laboratory, Richland, Washington.

Gerry, W. M. 1997a. *Calibration of Mass Flow Controllers*. SNF-TP-012, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Gerry, W. M. 1997b. *Calibration of Balzer Quadstar Mass Spectrometer*. SNF-TP-014, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Gerry, W. M. 1997c. *Calibration of MTI Gas Chromatograph Model M200*. SNF-TP-013, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Serles, J. A. 1997. *Furnace Testing of N-Reactor Fuel Element 3128W*. PTL-170, Revision 0, Pacific Northwest National Laboratory, Richland, Washington.

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)

Drying Results of K-Basin Fuel Element 1990 (Run 1)

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

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

Drying Results of K-Basin Fuel Element 5744U (Run 4)

Drying Results of K-Basin Fuel Element 6603M (Run 5)

Drying Results of K-Basin Fuel Element 1164M (Run 6)

Drying Results of K-Basin Fuel Element 2660M (Run 7)

Drying Results of K-Basin Fuel Element 6513U (Run 8)

Distribution

No. of
Copies

No. of
Copies

OFFSITE

C. L. Bendixsen
Idaho National Engineering and
Environmental Laboratory
P.O. Box 1625
Mail Stop 3135
Idaho Falls, ID 83415

A. W. Conklin
Washington State Department of Health
Airdustrial Park
Building 5, Mail Stop LE-13
Olympia, WA 98504-0095

M. A. Ebner
Idaho National Engineering and
Environmental Laboratory
P.O. Box 1625
Mail Stop 3114
Idaho Falls, ID 83415

A. R. Griffith
U.S. Department of Energy, Headquarters
19901 Germantown Rd (EM-65)
Germantown, MD 20585-1290

T. J. Hull
U.S. Department of Energy, Headquarters
19901 Germantown Road (EH-34)
Germantown, MD 20874-1290

M. R. Louthan
Savannah River Technology Center
Materials Technology Center
Aiken, SC 29808

T. E. Madey
Rutgers University
Bldg. 3865
136 Freylinghuysen Rd
Piscataway, NJ 08854

B. K. Nelson
U.S. Department of Energy, Headquarters
19901 Germantown Road (EM-65)
Germantown, MD 20874-1290

R. G. Pahl, Jr.
Argonne National Laboratory
P. O. Box 2528
Idaho Falls, ID 83403

R. S. Rosen
Lawrence Livermore National Laboratory
20201 Century Blvd., 1ST Floor
Germantown, MD 20874

D. Silver
Washington State Department of Ecology
P.O. Box 47600
Olympia, WA 98504-7600

T. A. Thornton
Yucca Mountain Project M&O Contractor
SUM1/423
1261 Town Center Drive
Las Vegas, NV 89134

No. of
Copies

No. of
Copies

ONSITE

6 DOE Richland Operations Office

R. M. Hiegel	S7-41
P. G. Loscoe	S7-41
C. R. Richins	K8-50
E. D. Sellers	S7-41
J-S. Shuen	S7-41
G. D. Trenchard	S7-41

24 Duke Engineering and Services,
Hanford, Inc.

C. B. Aycock	R3-11
R. B. Baker	H0-40
D. W. Bergmann	X3-79
S. A. Chastain	H0-40
D. R. Duncan	R3-86
J. R. Frederickson	R3-86
L. H. Goldmann	R3-86
S. L. Hecht	HO-40
L. A. Lawrence (5)	H0-40
P. J. MacFarlan	H0-40
B. J. Makenas	H0-40
R. P. Omberg	H0-40
R. W. Rasmussen	X3-85
A. M. Segrest	R3-11
J. A. Swenson	R3-11
C. A. Thompson	R3-86
D. J. Trimble	H0-40
D. J. Watson	X3-79
J. H. Wicks, Jr.	X3-74
SNF Project Files	

3 Fluor Daniel Hanford

E. W. Gerber	R3-11
D. A. Smith	T4-13
M. J. Wiemers	R3-11

2 Fluor Daniel Northwest

L. J. Garvin	R3-26
G. A. Ritter	H0-40

7 Numatec Hanford Company

G. P. Chevrier	H5-25
T. Choho	R3-86
E. R. Cramer	H0-34
T. A. Flament	H5-25
J. J. Irwin	R3-86
C. R. Miska	R3-86
J. P. Sloughter	H5-49

COGEMA Engineering Corporation

A. L. Pajunen	R3-86
---------------	-------

2 Technical Advisory Group

J. C. Devine	R3-11
R. F. Williams	R3-11

32 Pacific Northwest National Laboratory

J. Abrefah (5)	P7-27
J. P. Cowin	K8-88
S. R. Gano	K2-12
W. J. Gray	P7-27
B. D. Hanson	P7-27
G. S. Klinger	P7-22
D. K. Kreid	K7-80
J. M. Latkovich	K9-44
S. C. Marschman (10)	P7-27
B. M. Oliver	P7-22
T. M. Orlando	K8-88
J. C. Wiborg	K7-74
Information Release (7)	