Apparatus for Dynamic Measurement of Gases Released from Materials Heated Under Programmed Temperature-Time Control

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by

J. W. Early and R. M. Abernathey

ABSTRACT

This apparatus, a prototype of one being constructed for hot-cell examination of irradiated nuclear materials, measures dynamic release rates and integrated volumes of individual gases from materials heated under controlled temperature-time programs. It consists of an inductively heated vacuum furnace connected to a quadrupole mass spectrometer. A computerized control system with data acquisition provides scanning rates down to 1 s and on-line tabular and graphic displays. Heating rates are up to 1300°C/min to a maximum temperature of 2000°C. The measurement range is about 10^{-6} to 10^{-2} torr-liter/s for H_2 , CH_4 , H_2O , N_2 , and CO and 10^{-8} to 10^{-2} torr-liter/s for He, Kr, and Xe. Applications are described for measurements of Kr and Xe in mixed oxide fuel, various gases in UO_2 pellets, and He in $^{238}PuO_2$ power and heat sources.

I. INTRODUCTION

This apparatus was developed primarily as a prototype for hot-cell measurement of fission-product Kr and Xe and other gases released under controlled heating conditions from Fast Breeder Reactor (FBR) experimental fuels. Such measurements provide information concerning their gas-retention properties and irradiation stability.

This report presents a detailed description of the apparatus, its operational features, and experimental evaluations of its capability to measure Kr and Xe in FBR mixed oxide fuel, various impurity gases in UO_2 pellets, and He in $^{238}PuO_2$ power and heat sources.

II. DESCRIPTION OF APPARATUS

The major components are (1) a vacuum furnace with vacuum locks for introduction and removal of samples, (2) a temperature-time programmer that controls an induction heater, (3) a vacuum pumping system, (4) a quadrupole mass spectrometer, and (5) an on-line data acquisition system. All components are commercial units except the furnace. Figure 1 shows the glovebox in which the furnace is located, the

mass spectrometer, and the data acquisition system. Induction heating is provided by a Lepel 30-kW, 100-kHz rf generator. A Datatrak, Model FGE 5110, programmer controls the generator. As shown in Fig. 2, the top and bottom vacuum locks of the furnace are evacuated by a 5-L/s diaphragm pump, a 60-L/s cryosorption pump, and a 25-L/s ion pump, used sequentially. These pumps are located directly below the furnace glove box and connect to the furnace vacuum locks with 1.5 m of 3.8-cm-diam stainless steel piping. The UTI Model 100C quadrupole mass spectrometer and the furnace are evacuated by a 125-L/s turbomolecular pump. All pumps are oil-free to avoid hydrocarbon background.

The vertical furnace, shown in Fig. 3, provides gravity introduction and removal of samples through vacuum locks. The furnace is maintained continuously at a high vacuum to provide low and stable gas blanks and capability for high sample throughput rates. The small furnace provides ease of operation and maintenance in a 91.4-cm x 91.4-cm x 61.0-cm glove box. The furnace tube is fused quartz, 3.68-cm o.d. and 25.4-cm tall. A 2.75-in-o.d. Conflat flange is

Fig. 1. Glove box, quadrupole mass spectrometer, and data acquisition system.

sealed to the tube at the top and bottom by double Vitron O-rings with connections between them as a guard vacuum. The seals have proven leak-free after many thermal cycles of the furnace. The furnace assembly is sturdy and capable of withstanding maintenance handling. The conflat flanges are sealed rigidly to the top and bottom vacuum locks. The O-ring seals take up small expansions of the heated furnace tube and any vibrations. The furnace tube is cooled by water flowing in a polycarbonate encasement tube. The furnace is supported by four stainless steel tubes that are water cooled because of

their close proximity to the 6-turn rf induction coil wrapped around the middle of the polycarbonate encasement tube.

Positioned at the center of the furnace tube is a 1.9-cm-o.d. and 15.2-cm-long tantalum crucible, shown in Fig. 4. The crucible is suspended freely from the upper vacuum lock to relieve thermal expansions. The vertical slots located directly above the lower portion of the crucible reduce the heat in this area induced by the rf field. The horizontal slot above the vertical slots reduces the axial flow of heat to the crucible supports.

Fig. 2. Pumping System

The funnel portion of the crucible catches the introduced sample and guides it to rest on a hinged, tungsten trap door at the center point of the induction coil. The trap door is held closed by a tungsten rod connected to the gate valve of the lower vacuum lock. Manual opening of the gate valve results in opening the crucible trap door, allowing the expended sample to fall through the gate valve to a hopper in the lower vacuum lock.

The center hinge part of the trap door is fabricated from a rolled tantalum tab on the crucible. The hinge pin is a 1.5-mm-diam tungsten carbide rod that does not fuse to the refractory metal components during high-temperature operation. The trap door assembly has operated satisfactorily for hundreds of samples. For operation at $> 1600^{\circ}\text{C}$ with plutonium-containing samples, a 0.1-mm tungsten liner is inserted into the crucible to prevent a plutonium-tantalum reaction.

The maximum sample size accepted is $\sim 1\text{-cm}$ diam $\times 1.6\text{-cm}$ length. The apparatus easily handles FBR fuel and insulator pellets having usual dimensions of 0.62-cm diam and 0.62-cm length.

The vacuum locks have O-ring sealed ports at their sides through which samples are introduced or

removed. Both locks have hoppers as sample receptacles. A trap door at the base of the upper hopper is linked mechanically to the vacuum-isolation gate valve. Opening the trap door allows the sample to drop into the furnace when the isolation valve is opened. The lower hopper is removed through the vacuum lock port to recover the expended sample. The gate valves on both upper and lower vacuum locks are actuated pneumatically to provide fast operation.

Line-of-sight of the furnace crucible is provided by a quartz window at the top vacuum lock. By optical pyrometry, the furnace is calibrated for temperature vs power setting to a repeatability of 4°C for the range of 1000 to 2000°C .

Components in the apparatus are constructed of low-outgassing materials. Type 304 stainless steel is used for most components and vacuum lines. Conflat copper gaskets are used except for Viton O-ring Seals at the gate valves, quartz furnace tube, and vacuum lock ports.

A 2- μ , high-flow, sintered stainless steel filter prevents passage of particles to the vacuum pumping system.

A Digital Equipment Corporation PDP-11/34 mini-computer system controls the quadrupole mass spectrometer, acquires on-line gas release data, and displays analytical results. The real-time minicomputer system consists of a central processor with 64-K words of memory, a dual RL01 hard disk-drive system capable of storing 2.5 million words, a fast 12-bit AD11-K A/D converter for analog mass-peak height acquisition, a DL11-K digital I/O interface for controlling the operation of the mass spectrometer, an LA-120 Decwriter terminal/printer that displays analytical results, and a KW11-K dual programmable clock for event timing. The on-line software is a timed task-swapping routine in which data acquisition and quadrupole mass spectrometer control are performed in an interrupt-driven manner. Data reduction, storage, and display are concurrent with data acquisition and mass spectrometer control events.

III. OPERATION OF APPARATUS

A. Operational Sequence

A blank is processed, using the same temperature-time program as sample(s), just prior to sample processing.

Fig 3. Furnace in glove box.

Fig. 4. Crucible assembly.

The general operational sequence follows.

- (a) Insert sample into upper vacuum lock.
- (b) Pump down upper and lower vacuum locks.
- (c) Drop sample into crucible by opening, then closing, the upper vacuum-lock isolation valve.
- (d) Heat sample, using preset temperature-time program, under computer control. Start data acquisition.
- (e) Drop sample from crucible by opening, then closing, lower vacuum lock.
- (f) Pressurize vacuum locks with dry nitrogen to atmospheric pressure.
- (g) Remove sample from lower vacuum lock.
This step usually is done simultaneously with step (a) during the heating operation of a previously loaded sample.

A usual gas-release elapsed time is 1 h with a range of 2 min to 48 h depending on the information desired. The stability of the overall system is sufficiently high to provide reproducible blank data for 72 h, thereby giving capability for a 24-h sample run preceded by a 24-h blank and an optional 24-h blank afterwards. For gases, such as He, that

are not blank components, 48-h sample runs have been used.

The time required to pump down vacuum locks to $\leq 5 \text{ E-6 torr}$ before insertion or removal of a sample is 15 to 25 min. At 5 E-6 torr , opening the vacuum locks does not affect the system blank significantly. A typical pumpdown sequence is operation of the diaphragm pump for 1 min to 10 torr, operation of the cryosorption pump for 15 min to 2 E-5 torr , and operation of the ion pump for 5 min to 5 E-6 torr .

B. Data Recording and Treatment

The mass spectrometer is programmed to scan and measure release rates of desired gases at typical intervals of 1 to 900 S. The fastest scan rate is 2 amu/s , limited by the response of the detector's electrometer.

The blank values, taken just prior to samples, are subtracted point-by-point in elapsed time from the sample values. Also subtracted are mass spectrometer baseline values.

After completion of a sample scan, the blank-corrected dynamic-release rates in units of torr-L/s and integrated volume in units of STP L for each gas are printed and graphed. Also printed are the accumulative (STP liter) volumes. Finally, the integrated volume of each gas is printed along with its computed volume percentage. A printed output and plot of a dynamic-release rate, of helium from a $^{238}\text{PuO}_2$ sample, are given in Table I and Fig. 5.

IV. CAPABILITIES OF APPARATUS

A. Measurement Range and Blank Values for Various Gases

The detection limit of the mass spectrometer generally is 1 E-8 torr-L/s for most gases, set by the noise level of the electron multiplier detector at the highest level of used amplifier gain. The blank levels of H_2 , CH_4 , H_2O , N_2 , and CO are above this detection limit. These gases are outgassed from various components in the furnace. Typical blank values of gases for a furnace-operating temperature range of 1400 to 1800°C are given in Table II. The variations in the blank values typically are $< 5\%$ over 24 h. The overall detection limits are taken as one-half the blank values as shown in Table II.

The maximum value measurable is about 1 E-2 Torr-L/s for the mass spectrometer used. Above this

TABLE I

PRINTED OUTPUT OF DYNAMICALLY RELEASED HELIUM

HELIUM

HE RELEASE RUN ID = 823
 HE FLOW SENSITIVITY = 3.106E-00004
 HE RUN START BLOCK = 03115
 HE RUN END BLOCK = 03117
 HE BLANK START BLK = 03107
 RUN START TIME = 16:07:16

ACCUMULATED VALUES

CURRENT SCAN VALUES

SCAN	STP VOL (L)	RELEASE RATE (T-L/S)	STP VOL (L)	TIME (SEC)
1	2.190E-00011	1.933E-00008	2.190E-00011	1
2	1.501E-00010	1.672E-00008	1.282E-00010	7
3	3.111E-00010	2.109E-00008	1.610E-00010	13
4	8.391E-00010	6.922E-00008	5.280E-00010	19
5	3.199E-00009	3.104E-00007	2.360E-00009	25
6	2.910E-00008	3.366E-00006	2.590E-00008	30
7	2.901E-00007	3.371E-00005	2.610E-00007	36
8	1.407E-00006	1.427E-00004	1.117E-00006	42
9	2.757E-00006	1.774E-00004	1.350E-00006	48
10	4.367E-00006	2.087E-00004	1.610E-00006	54
11	6.207E-00006	2.375E-00004	1.840E-00006	60
12	8.217E-00006	2.636E-00004	2.010E-00006	66
13	1.041E-00005	2.858E-00004	2.190E-00006	72
14	1.264E-00005	2.909E-00004	2.230E-00006	77
15	1.487E-00005	2.946E-00004	2.230E-00006	83
16	1.690E-00005	2.599E-00004	2.030E-00006	89
17	1.860E-00005	2.221E-00004	1.700E-00006	95
18	2.008E-00005	1.899E-00004	1.480E-00006	101
19	2.135E-00005	1.623E-00004	1.277E-00006	107
20	2.243E-00005	1.384E-00004	1.076E-00006	113
21	2.335E-00005	1.181E-00004	9.280E-00007	119
22	2.414E-00005	1.008E-00004	7.880E-00007	125
23	2.482E-00005	8.567E-00005	6.730E-00007	131
24	2.539E-00005	7.324E-00005	5.730E-00007	137
25	2.588E-00005	6.256E-00005	4.880E-00007	143
26	2.629E-00005	5.336E-00005	4.140E-00007	149
27	2.664E-00005	4.542E-00005	3.510E-00007	154
28	2.694E-00005	3.859E-00005	3.030E-00007	160
29	2.702E-00005	3.285E-00005	2.550E-00007	166
30	2.742E-00005	2.782E-00005	2.180E-00007	172
31	2.760E-00005	2.348E-00005	1.840E-00007	178
32	2.777E-00005	2.172E-00005	1.700E-00007	184
33	2.792E-00005	1.855E-00005	1.450E-00007	190
34	2.804E-00005	1.586E-00005	1.230E-00007	196
35	2.815E-00005	1.357E-00005	1.076E-00007	202
36	2.824E-00005	1.157E-00005	9.050E-00008	208
37	2.832E-00005	9.861E-00006	7.730E-00008	214
38	2.838E-00005	8.421E-00006	6.650E-00008	220
39	2.844E-00005	7.178E-00006	5.690E-00008	226
40	2.849E-00005	6.117E-00006	4.760E-00008	232
41	2.853E-00005	5.194E-00006	4.030E-00008	238

Fig. 5. Plot of dynamically released helium.

for samples (and blanks). The variations typically are less than 3% over 160 h of operating time. The evaluation of the overall reliability of the complete apparatus is difficult to establish. The best technique would be to heat well-characterized reference materials, especially those of the National Bureau of Standards (NBS). Unfortunately, the only NBS reference materials are metals that would melt and damage the furnace.

Reliability estimates were obtained by flowing N_2 (a known blank component) and He (not detected in blanks) at rates from about 10 to 1000 times the detection limit for various elapsed times and comparing the measured integrated volumes to the input volumes (Table III). The precision (relative standard deviation) and biases were consistently $< 2\%$.

C. Limitations Caused by Reactions with Furnace Materials

A chronic problem associated with construction of furnaces used for gas-release measurements is reaction of furnace materials with various gases. For operation at temperatures to 2000°C , there is no material that is mechanically stable and does not react with many gases present in nuclear fuels. Tantalum and tungsten were selected as the furnace component materials based on their mechanical stability and inertness to many gases. These two metals

flow rate, the flow-sensitivity factors decrease because of space-charge effects in the ionizer section.

B. Establishment of Flow-Sensitivity Factors

The flow-sensitivity factors are established by flowing pure gases at known rates into the mass spectrometer operated at the conditions to be used

TABLE II
TYPICAL BLANK VALUES AND DETECTION LIMITS

Gas	Torr - L/s E-6 at Temperature of			Detection Limits (Torr-L/s) at 1800 °C
	1400°C	1600°C	1800°C	
H ₂	0.60	0.80	1.6	8E-7
He	<0.1	<0.1	<0.1	<5E-8
CH ₄	<0.1	<0.1	<0.1	<5E-8
H ₂ O	0.15	0.17	0.17	9E-8
CO	0.80	1.0	1.3	7E-7
N ₂ ^(a)	<0.1	0.16	0.16	8E-8
Kr	<0.1	<0.1	<0.1	<5E-8
Xe	<0.1	<0.1	<0.1	<5E-8

(a) At the detection limit, N₂ and CO are indistinguishable

TABLE III
PRECISION AND ACCURACY FOR He AND N₂

Gas	Avg Flow Torr-L/s	Input Vol, Std cm ³	Measured Vol, Std cm ³	Number of Tests	Std Dev, Rel %	Avg Bias, %
He	2.6 E-7	7.07 E-5	6.92 E-5	5	1.8	- 2.1
He	2.7 E-6	7.07 E-4	7.04 E-4	4	0.6	- 0.4
He	1.8 E-5	7.07 E-3	7.02 E-3	4	0.8	- 0.7
He	1.7 E-4	7.07 E-2	7.05 E-2	4	1.5	- 0.3
N ₂	7.1 E-7	3.54 E-4	3.46 E-4	4	0.5	- 2.2
N ₂	7.7 E-6	3.54 E-3	3.61 E-3	4	1.0	+ 2.0
N ₂	7.9 E-5	3.54 E-2	3.56 E-2	4	0.7	+ 0.6

react with O₂ to form oxides, with H₂O to form oxides and H₂, and with CH₄ to form carbides and H₂.¹⁻³ The reactions are dependent on temperature and surface condition of the metals in a complex manner. Correction for these reactions is, therefore, difficult. The extents of the reactions of O₂, CH₄, and H₂O were measured for the furnace starting with clean metal surfaces. The three gases were introduced individually into the furnace at known rates over a temperature range of 25 to 1800°C. The fraction of gas that reacted was computed based on the rate measured by the mass spectrometer. As shown in

Fig. 6, the reaction order is O₂ > H₂O > CH₄. This, then, also is the measurement uncertainty order for samples. Because the reaction of H₂O and CH₄ with tantalum and tungsten produces H₂, measurement of H₂ also is uncertain when these gases are present. Because the reactions are dependent on surface conditions of the metal components, corrections require calibrations just prior to and just after sample processing. Extensive experimentation to establish the reliability of such corrections has not been done. With clean metal surfaces, the reaction rates shown in Fig. 6 were reproducible to $\pm 10\%$.

Fig. 6. Reactions of oxygen, water, and methane with furnace.

D. Determination of Response Time

To minimize constriction effects, all vacuum piping and particle-entrainment filters were fabricated to have high conductance. To demonstrate the effectiveness of the apparatus to measure dynamically a sudden gas release, a known flow of N₂ was introduced suddenly into the furnace. The elapsed time between the release of the N₂ and its detection at the quadrupole mass spectrometer was less than 1 s at a flow rate of 1E-6 torr-L/s. This response, comparable to the fastest scan rate of the spectrometer, is acceptable.

V. APPLICATIONS

A. Determination of Kr and Xe in FBR Fuel

Experiments with the prototype have shown that Kr and Xe isotopes are measured with ample sensitivity for application to retained-gas analysis of FBR fuel.⁴ The low-abundance fission-yield isotopes ⁸⁴Kr and ¹³¹Xe were measured with ample sensitivity to determine 10% retained Kr and Xe in 1 g of Pu having 1% burnup. The integrated volumes measured for constant rate flows over a 1.5-h elapsed time were 3E-4 std cm³ of ⁸⁴Kr and 3.5 E-3 std cm³ of ¹³¹Xe. For FBR mixed oxide fuel, the quantity of ⁸⁴Kr will be greater.

B. Determination of Gases Released from UO₂ Pellets

Pellets of UO₂ from a batch that had been prepared by calcination of uranium oxide with a carbowax binder at 1600°C in a steam-H₂ atmosphere were processed. Four pellets were processed at 1400°C, four at 1600°C, and three at 1800°C. The elapsed time for > 99% release of all gases was 1 to 1.5 h. The measured integrated quantities of H₂, H₂O, CH₄, CO, and N₂ are plotted in Fig. 7. The standard deviations are represented by error bars. Pure gases were not processed through the furnace to enable corrections with furnace components. Therefore, the data represent the combinations of released gases and their reactions.

The increase in CO with increase in temperature is attributed to its formation by reaction of residual carbonaceous matter with UO₂, $C + 2 UO_2 \rightarrow CO + U_2O_3$. Another mode of formation may be reaction of CH₄ with UO₂, $CH_4 + 6 UO_2 \rightarrow CO + 3 U_2O_3 + 2 H_2O$, indicated by the decrease in CH₄ and increase in H₂O with increasing temperature. Undoubtedly, the

Fig. 7. Gases released from UO₂ pellets.

released H_2O reacts with metal components of the furnace to produce H_2 . However, the amount of H_2 formed by this reaction is small relative to the amount of H_2 initially present in the pellets. The low amount of N_2 released is evidence of low amounts of air in the pellets. The apparent increase in N_2 released with increasing temperature, which parallels the CO release, probably reflects imperfect cracking-pattern factors for equal mass CO and N_2 .

C. Determination of He Released from $^{238}PuO_2$ Power and Heat Sources

The applicability of the apparatus to measure He, the alpha-decay product of plutonium and uranium isotopes, was demonstrated initially on a batch of FBR mixed-oxide fuel pellets. Seven 5-yr-old pellets were processed at $1800^\circ C$. The integrated amounts of helium released ranged from 0.0023 to 0.0032 std cm^3/g .

The apparatus was used to measure the He released from a large number of $^{238}PuO_2$ space power and heat sources using a variety of heating conditions. Heating rates ranged from $10^\circ C/min$ to $1300^\circ C/min$ for elapsed times of 2 min to 48 h. A typical heating profile that simulates the temperature change undergone upon atmosphere reentry is given in Fig. 8. The dynamic plot of He release for this heating mode is shown in Fig. 9. To ensure total release of He, the programmed heating is ended with an isothermal heating at 1600 to $1800^\circ C$ until the He release decreases to insignificance.

The quantity of $^{238}PuO_2$ processed ranged from 0.04 to 3 g. The total amount of He released ranged from 0.009 to 4 std cm^3 . The measured total released He has agreed closely and consistently with the He calculated from radioactive decay.

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Fig. 8. Typical heating profile for $^{238}PuO_2$ power source.

Fig. 9. Plot of dynamically released helium from reentry heating profile.

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