RESIDUAL AND FISSION GAS RELEASE FROM URANIUM DIOXIDE

By

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ABSTRACT

Residual and fission gas release from UO_2 were studied in the laboratory and in in-reactor experiments. Arc-fused powder and sintered pellets were used to determine the rate of evolution and types of residual gases as a function of temperature.

Fission gas release was related to the average UO_2 temperature prevalent in fuel elements studied during irradiation. The UO_2 temperature and fission gas release calculations were made using the latest thermal conductivity values, isotopic half lives, and branching ratios available in the literature. The results obtained were compared with those available in the literature, and a satisfactory agreement was found among the groups of comparable data.

I. INTRODUCTION

Three different physical forms of uranium dioxide are either already in use or being considered for use as fuel for commercial power reactors. The three kinds of UO_2 are: (1) sintered pellets prepared from ceramic grade UO_2 , (2) compacted UO_2 powder (usually arc-fused), and (3) coated UO_2 particles dispersed in graphite, in other ceramic materials, or in a metallic matrix. Sintered pellets have been used in significantly larger quantities than the other two types. The relative merits of these three types of fuel have not yet been established, because no significant performance data are available for compacted UO_2 and coated UO_2 . In view of potential cost advantages of the powder compaction methods, considerable work is being done to develop the required fuel technology.

In all three fuel types, structural support and protection against corrosion and erosion are provided the UO_2 by enclosing it in gas-tight metal sheaths. During irradiation various gaseous impurities have been found to escape from the UO_2 fuel charge into the available void volume inside the sheath. These impurities include both fission-produced gases and residual gases that have been introduced into UO_2 during the course of fuel element fabrication.

Fuel element performance can be affected by the gaseous impurities through the generation of high internal pressure, the reduction of thermal conductivity of the gas surrounding the UO_2 , or a side reaction of the gaseous impurities with the sheath. For this reason, data on the generation and release of these gases from the UO_2 , as well as information on methods of reducing the quantities of gases and gas-producing impurities in UO_2 , are important to the fuel designer.

II. SUMMARY AND CONCLUSIONS

The gaseous impurities contained in UO_2 reactor fuel are of two general types: (1) residual gases, which are introduced in the fuel fabrication process as sorbed gases, or as liquids or solids that form gases thermally during irradiation, and (2) fission gases, which are generated as the nuclear products of fissionable isotopes.

The quantities and analyses of residual gases were studied by vacuum outgassing both sintered pellets and samples of arc-fused powder at temperatures ranging from 200 C to 1700 C. At 1500 C to 1700 C, the major portion of these gases was released from both pellets and powder within the first 10 minutes of outgassing. The total residual gas content of the pellets was found to be not greater than 10 microliters per gram of UO_2 . The major constituents were hydrogen and carbon monoxide. Arc-fused powder was found to contain as much as 750 microliters of residual gas per gram. Nitrogen, hydrogen, and carbon monoxide were the gases present in greatest quantities in this case.

Vacuum outgassing at the relatively low temperature of 800 F (427 C) followed by purging with pure helium has proved an effective means of removing residual gaseous impurities from sintered pellets. Sintering arc-fused powder at 1650 C in a hydrogen atmosphere can reduce the residual gas content considerably, but the effectiveness of this process decreases with increasing size of UO_2 particles.

Fission gas release from UO_2 during irradiation has been studied at the Atomic Power Equipment Department and at other sites. (1, 2, 3, 4, 5) Gas diffusion kinetics for UO_2 temperatures below 1650 C are fairly well understood, but only fragmentary quantitative information for gas evolution above this temperature level is available. The results of a number of irradiation experiments conducted with test fuel assemblies in the Vallecitos reactors have provided design data on the release of gases from sintered UO_2 pellets during irradiation at relatively high temperatures. The temperature dependence of fission gas release is the main concern of this portion of the paper.

When irradiation of a given assembly had been completed, the quantity of fission gas released was determined for various fuel rods by puncturing the stainless steel or Zircaloy tubing encapsulating the pellets, collecting the gas in an all-glass vacuum apparatus, and analyzing the gas by gamma counting of Kr^{85} and/or chromatographic techniques. These release values then were combined with calculated values of gas generated during irradiation to determine the percentages of fission gas released.

The heat flux at which a given rod operated was calculated from the amount of uranium burned up, the energy produced per fission, the length of time the reactor was at power during the irradiation period, and the rod geometry. Recently acquired data on thermal conductivity were applied to calculate UO_2 centerline temperatures from the heat flux values. (6)

Percent fission gas release was plotted as a function of UO_2 temperature for average center-line temperatures up to approximately 4000 F. The average terminal burnup values for the fuel assemblies considered ranged from 121 to 5000 megawatt days per short ton of uranium metal. The data indicates the possibility of 50 to 60 percent of generated fission gases being released between 3500 F and 4000 F.

The results obtained from these experiments on fission gas release were compared with those obtained by other investigators. Data determined by direct internal fuel pressure measurements were included in this comparison. In view of the variations in experimental procedure, the degree of agreement was satisfactory.

III. RESIDUAL GAS RELEASE FROM UO_2

The amounts and types of residual gases contained in uranium dioxide reactor fuel depend upon the method of fuel preparation. A brief description of the final steps of the usual fabrication techniques for the three types of fuel is given below:

a. Pellets

Ceramic-grade UO_2 powder is pressed into green pellets. The pellets are sintered in a hydrogen atmosphere to 0.94 of theoretical UO_2 density. In many cases, pellets are ground under water and then dried in air. The pellets are then loaded into metal tubes.

b. Powder (arc-fused or equal)

The particles of UO_2 powder are in crystalline form and usually 0.98 to 0.99 of theoretical UO_2 density. The particles are loaded into the cladding tubes and either vibrationally compacted to approximately 0.87 bulk density or compacted by a combination of vibration and swaging of the cladding to a bulk density of 0.92 to 0.93. Some outgassing steps are usually performed before loading to remove certain residual gases.

In both cases a and b above, the air in the fuel element cavity is replaced with helium, mainly for the purpose of improving heat transfer, but also for the purpose of allowing mass spectrometer leak testing subsequent to the welding of end closures.

c. Coated Particles

Particles of UO_2 usually are coated by vapor deposition of graphite or other ceramic-type layers. In cermet matrices, the UO_2 is mixed with metallic powder, pressed, sintered, and rolled to suitable sizes.

In order to determine the nature of residual gases present in the different forms of UO_2 fuel and the conditions required for their removal, a series of laboratory outgassing experiments was conducted. Because of the diverse methods of preparation, the studies reported in this section were divided into separate categories for pellets and powders. The problems relative to residual gases in arc-fused and coated-particle grades are similar and will be discussed collectively.*

A. EXPERIMENTAL PROCEDURE

1. Sample Preparation

a. Sintered Pellets

Pellets used in these experiments were made from ceramic grade UO_2 , cold pressed and sintered at 1600 C in a dry hydrogen atmosphere to densities higher

* Fission gas release from coated particles has been reviewed recently by G. W. Cunningham in "Reactor Materials" Volume 6 No. 1, February 1963, page 1.

than 0.94 of UO_2 theoretical. The pellets were ground under water and air-dried at 225 F to 250 F. Open porosity for pellets made by sintering was measured by water and helium immersions, and found to be about 0.2 to 0.4 percent. (7)

One group of pellets was fabricated without employing a binder in the powder pressing step. In the fabrication of a second group, approximately 1 to 3 percent by weight of a paraffin wax binder was added during the ball milling operation. All other operating steps were identical for both groups.

A chemical analysis of the pellets used in the residual gas release experiments is shown in Table I.

b. Arc-Fused UO_2 Powder

Arc-fused UO_2 powder was obtained from commercial sources, or produced at APED by arc-fusing ceramic grade powder. Three separate batches of powder were used in the outgassing experiments. In any case, the oxygen-to-uranium ratio was maintained near 2.00 in the finished product. A typical chemical analysis for powder used in these experiments is given in Table II.

Outgassing experiments were conducted both with samples in the "as arc-fused" state and with samples processed further through a sintering operation. The sintering operation consisted of cycling the arc-fused powder through a furnace at 1650 C for 1 hour in a hydrogen atmosphere.

2. Outgassing Procedure*

UO_2 pellets and powder samples were outgassed in a vacuum at temperatures ranging from 200 C to 1700 C by using the hot extraction furnace on a National Research Corporation gas analyzer. Briefly, the method was as follows: The sample was heated by induction in a vacuum ($< 1 \times 10^{-6}$ mm Hg), and the gases were transferred by means of two mercury diffusion pumps and a Toepler pump into a precision four-range McLeod Gauge. There the pressure reading was taken, and the total amount of gas was calculated. Each sample was dumped from the crucible after the analysis was made so that there was no outgassing blank from the previous samples. The weight of the samples necessary for accurate gas collection, measurement, and analysis was determined to be 10 to 12 grams for pellets and approximately 10 grams for arc-fused powder.

Studies of the rate of gas expulsion were made by pumping the gas removed into the McLeod Gauge approximately every 5 minutes and taking pressure readings. The composition of the gases expelled was analyzed by mass spectrometric and gas chromatographic methods.

* H. E. Perrine, Nuclear and Inorganic Chemistry, VAL.

TABLE I**CHEMICAL ANALYSIS OF PELLETS***

Al	10 ppm
Bi	< 2
B	25
Cd	< 5
Ca	10
Cr	20
Co	< 5
Cu	2
Fe	100
Pb	1
Mg	35
Mn	10
Mo	5
Si	60
Ag	0.1
Na	< 35
Sn	< 1
V	< 15
Zn	20
Ni	20
Sb	< 2
C	27
F	44
U-235	2.6%
O/U	2.001

* Binder used in one group of pellets did not change the chemical analysis.

TABLE IITYPICAL CHEMICAL ANALYSIS, ARC-FUSED UO_2

<u>Element</u>	<u>Concentration</u>	<u>Element</u>	<u>Concentration</u>
Al	10 ppm	Si	10 ppm
Bi	1	Ag	1
B	< 0.2	Na	< 35
Cd	< 1	Sn	< 1
Ca	< 2	V	< 15
Cr	100	Zn	20
Co	< 5	Sb	< 2
Cu	2	Ni	10
Fe	20	Ti	50
Pb	1	W	10
Mg	1	Ta	< 1.0
Mn	< 1	C	40
U (free metal)	1300	Cl	< 10
		F	< 10

O U = 2.001

Particle density = 10.806 gm cc

Enrichment = 4.03 $\pm$ 0.06 percent U-235

B. OUTGASSING TEST RESULTS

1. Pellets

The importance of temperature in the outgassing of pellets is shown by Figure 1. In a 30- to 40-minute outgassing period both the rate of gas expulsion and the total volume of gases expelled increased with increasing temperature within the range of study. ⁽⁸⁾ Outgassing at 200 C in vacuum resulted in a total gas release of only 0.02 microliters per gram. A two-temperature step outgassing procedure in which the pellets were held at 400 C for 15 minutes, and then at 1500 C for 30 minutes resulted in a lower total gas expulsion than that attained by single-step outgassing at 1500 C. The latter procedure proved nearly as effective as 1700 C outgassing. At both 1500 C and 1700 C almost all of the total gas release occurred during the first 7 minutes of outgassing. From the lower set of curves of Figure 2 it appears that the use of a binder in the pressing of pellets had no effect on the release of residual gases.

Analyses of the gases emitted during pellet outgassing at different temperatures is given in Table III. The principal constituents were found to be hydrogen, helium, and carbon monoxide. The large percentage of helium was caused by storing the sintered pellets in a helium atmosphere.

2. Powder

The results of powder outgassing are shown in Figures 2 and 3. The effect of temperature is indicated by the curve of Figure 3. In this experiment samples from a single batch of as-fused powder were outgassed at various temperatures for 30 minutes. A second batch of powder was used in the 48-hour experiments at 900 C. In this particular test, samples that had been pulverized and ball milled showed only small increases in residual gas release when compared with swaged samples.

Thirty-minute outgassing experiments at 1700 C were conducted on samples from the third powder batch in order to determine the effect of sintering the arc-fused powder at 1650 C in hydrogen prior to outgassing. The upper two curves of Figure 2 show that a reduction in gas content from approximately 400 microliters per gram to nearly 150 microliters per gram was accomplished by sintering this particular batch. A similar series of experiments on still different lots of arc-fused powder has been reported in another document. ⁽⁹⁾ In this series 4 percent enriched powder was sintered in a hydrogen atmosphere at 1650 C. With one batch, such a treatment reduced the total gas content from approximately 550 down to 18 microliters per gram of UO_2 , as determined by vacuum extraction at 1500 C. In a test on a sample of the second batch, however, the same sintering operation failed to reduce the gas content by any significant quantity. The difference in behavior of the two batches was attributed to the difference in particle size distribution. This reasoning follows from the fact that the escape of gas from UO_2 is diffusion dependent.

The importance of powder preparation in residual gas content is indicated by a comparison of Figures 2 and 3. Tests on the powder batch corresponding to the curve of Figure 3 indicate a content of some 750 microliters per gram, almost twice the gas content of the "as-fused" sample used in the 1700 C outgassing experiment (Figure 2).

Table IV gives the gas analyses of "as-fused" samples outgassed at 900 C for 48 hours and of powder samples that were given the sintering treatment and then outgassed at 1700 C for 30 minutes. Approximately one-half of the gas content of the first set of samples was nitrogen, and considerable hydrogen was also present. On the other hand, one-half to two-thirds of the gas content of the "sinter treated" powder was carbon monoxide. Again, hydrogen was present in very significant quantities.

Figure 1. Outgassing of UO_2 Sintered Pellets
Effect of Temperature.

Figure 2. Outgassing of Pellets and Powder

TABLE III
GASES RELEASED FROM SINTERED UO_2 PELLETS PRESSED WITH A BINDER
 Microliters of Gas Per Gram of UO_2 (NTP)

Sample No.	Outgassing Temp. (°C)	Total Gas Expelled	H ₂	He	O ₂	H ₂ O	CO ₂	A	N ₂	CO	CH ₄	Hydrocarbons C ₂ - C ₅
--	400	1.64	0.48	NA	0.02	0.06	0.51	NA	0.15	0.32	0.05	
--	400 (15 min)	6.89	2.70	NA	Tr.	Tr.	0.49	NA	1.05	2.47	0.29	
	1500 (30 min)											
1	1700	8.10	NA (Not Analyzed)									
2	1700	7.50	1.21	4.41	0.02	0.08	0.04	0.01	0.02	1.02	0.02	Tr.
3	1700	8.94	2.53	2.94	Tr.	0.63	0.12	Tr.	0.39	2.29	0.03	< 0.04
4	1700	8.28	1.89	3.02	0.02	1.33	0.06	Tr.	0.18	1.70	0.03	< 0.04
6	1700	8.06	1.35	NA	ND	NA	NA	NA	ND	1.00*	0.94*	NA
8	1700	8.33	2.84	NA	ND	NA	NA	NA	ND	1.01*	1.08*	NA
10	1700	8.35	1.50	NA	ND	NA	NA	NA	ND	0.08*	1.30*	NA
18	1700	10.43	1.33	NA	ND	NA	NA	NA	ND	0.54*	0.58*	NA

*CO and CH_4 identified as one peak which could not be resolved.

- Notes:
1. (NTP) - Normal Room Temperature 22 - 23 C, and atmospheric pressure.
 2. 1000 Microliters = 1cc
 3. NA = Not analyzed
 4. ND = Below the limits of detection
 5. Tr. = Trace quantity

Figure 3. Outgassing of Arc-fused UO₂

TABLE IV

GASES RELEASED FROM ARC-FUSED UO_2 POWDERMicroliters of Gas Per Gram of UO_2 (NTP)

Sample No.	Outgassing Temp ($^{\circ}\text{C}$)	Outgassing Time (hr)	Total Gas Expelled	H_2	He	O_2	H_2O	CO_2	A	N_2	CO	Hydrocarbons
B-13-1	900	48	585	33.6	0.28	0.077	NA	< 0.005	< 0.006	340	NA	NA
B-13-2	900	48	593	78.5	0.17	0.077	NA	1.53	< 0.006	304	NA	NA
B-13-3	900	48	533	67.2	0.45	0.070	NA	1.53	0.067	272	NA	NA
200-1	900	48	613	78.5	0.34	0.7	NA	1.02	< 0.006	312	NA	NA
200-2	900	48	617	112.	0.28	0.007	NA	1.02	< 0.006	296	NA	NA
--	1700	0.5	149.3	51.7	NA	0.12	Tr.	16.8	NA	4.3	74.2	3.0
--	1700	0.5	158.2	19.9	NA	0.6	Tr.	6.1	NA	10.8	101.4	< 1.6

Notes:

1. Samples B-13-1, -2, and -3 are -20 mesh fused UO_2 from a swaged rod with prewelded ends
2. Samples 200-1 and -2 are fused UO_2 which has been pulverized by hammer milling and ball milled
3. Samples outgassed at 1700 C for 30 minutes were sintered for one hour at 1650 C in a hydrogen atmosphere prior to outgassing.

IV. FISSION GAS RELEASE FROM UO_2

Approximately 30 percent of the fission products of uranium are gases, primarily the stable isotopic species of xenon and krypton. The rate of fission gas production in a UO_2 fuel element is about 1.35×10^{-3} gram-mole per megawatt-day of energy produced. Thus, by the time the fuel has reached an exposure of 10,000 megawatt-days per ton of uranium, 300 cubic centimeters (STP) of gas will have been generated for each kilogram of UO_2 .

The release of fission-produced gases from the uranium dioxide to the free volume of the surrounding sheath is a function of the initial density, the degree of deviation from stoichiometry, the exposure, or burnup, level, and the temperature of the UO_2 .⁽⁴⁾ The temperature dependence of fission gas release is the factor of prime interest taken up in this section. Although the kinetics of gas diffusion are fairly well understood for UO_2 temperatures below 1650 C, very little quantitative information on the escape of gases above this temperature level has been available. The results of a number of irradiation tests conducted in both the Vallecitos Boiling Water Reactor (VBWR) and the General Electric Test Reactor (GETR) provide design data on the release of fission gas from pelleted UO_2 subjected to relatively high temperatures.

A. IRRADIATION EXPERIMENTS AND ANALYTICAL TECHNIQUES

1. Pre-Irradiation Fuel Data

Information on fission gas release was obtained from the irradiation testing of the following fuel elements. (10, 11)

<u>Element Designation</u>	<u>Number of Fuel Rods</u>
S-I-1-B-P (formerly S1-a)	16
S-II-2-G-P	9
S-II-3-G-P	9
PWL-6	5
DP-1	9
DP-5	9
DP-14	9
NUSU	1 (annular type)

The fuel rods consisted of sintered UO_2 pellets encapsulated by either stainless steel or Zircaloy-2 tubing. The active fuel lengths ranged from 34 inches to 37 inches. Pellets were 0.40 inch to 0.50 inch in diameter, except in the case of the annular pellets contained in the NUSU element. The ID and OD of these annular pellets were 1.0 and 1.5 inches. UO_2 densities fell between 92 percent and 96 percent of theoretical, and chemical analyses of sample pellets showed the ratios of oxygen to uranium to be 2.00 to 2.02. The UO_2 used in the elements S-II-2-G-P, S-II-3-G-P, DP-1,

DP-5, and DP-14 originated from the same batch of powder and were pressed and sintered under identical conditions. The clearances between pellets and cladding wall were 0.007 inch or less in all cases.

2. Irradiation Test Data

The fuel rods were irradiated at maximum heat fluxes of 130,000 to 420,000 Btu/hr-ft² to average burnup levels up to 5000 MWD per short ton of uranium. Figure 4 shows a neutron flux profile typical of an element irradiated in the VBWR. Such profiles were determined by gamma scanning the elements and rods at the end of irradiation life.

The VBWR operated with a nearly constant neutron flux distribution but at a variable power level. As a rule, the irradiation histories of elements tested in this reactor show operating time at several levels of power and numerous power cycles, for example, 40 such cycles for DP-1, and 80 for both DP-5 and DP-14. Hence, the ratio of peak heat flux to average flux along the length of a given fuel rod, as well as the location of the peak, were nearly constant, but the magnitudes of these fluxes were subject to considerable variations. Among the different rods irradiated the peak-to-average flux ratios ranged from 1.2 to 1.6. Irradiation tests were scheduled so that the fuel elements would operate at maximum power near the end of the tests. Data on VBWR operation during the irradiation of element S-II-2-G-P are presented as an example in Table V. A plot of reactor thermal power versus time for the final run of the series is shown in Figure 5.

One test assembly, PWL-6, was irradiated in the Pressurized Water Loop (PWL) of the GETR. This assembly was subjected to seven power cycles but was held at a single power level during the time of reactor operation, as shown in Figure 6. In general, the neutron flux distribution varied somewhat during a GETR cycle of operation. The typical result was an upward shifting of the peak by a few inches combined with a flattening of the peak from a maximum P/A (Peak/Average) ratio of approximately 1.6.

3. Collection and Analysis of Fission Gas

After the irradiation of a fuel bundle had been completed, it was transferred from the reactor to a hot cell at the Radioactive Materials Laboratory and disassembled. In order to determine the amount of free fission gas in a fuel rod, the rod was placed in a puncturing station, shown in Figure 7. The fuel rod surface was sealed vacuum tight to the puncture device, and the pressure in the entire gas collection system was reduced to about 100 microns. A hydraulically driven needle was forced through the cladding wall and then withdrawn. The free gases within the fuel rod flowed by pressure difference through the puncture head, a particulate filter, a -30 F iodine trap, and to the out-of-cell gas collection flask until the pressure was equalized. Since the collection system volume was large compared to the free volume of the rod, the ratio of the

volume of the glass flask to the volume of the system was taken as the volume fraction of gas collected. When the activity of the original sample in the counting flask was high, it was diluted by one or more calibrated expansions. In some cases, Kr carrier gas was added to increase the sample bottle pressure for added dilution expansions. (11, 12, 13)

In order to analyze the gas by the gamma counting technique, an aliquot of the collected gas was transferred to the counting cell of a 256-channel gamma spectrometer (Na I crystal). Counting was based on the 0.52-Mev gamma rays associated with krypton-85 decay. The percentage of disintegrations resulting in gamma rays of this energy had been determined to be 0.35 ± 0.07 percent. ⁽¹⁴⁾ With this information it was thus possible to calculate the number of Kr-85 atoms which had been released from the UO_2 lattice.

An alternate method of analyzing the gases collected was that of gas chromatography. A sample of the gas mixture was admitted to an evacuated small glass container attached to the chromatograph. The sample was then carried by flowing helium from the container into the chromatograph, which employed columns of either molecular sieves or silica gel. Determination of Kr and/or Xe was performed by using calibration curves, employing either peak height or peak area correlation. Stable Kr and Xe were used for calibration. ⁽¹³⁾

4. Determination of U Burnup, Fission Gas Production, and UO_2 Temperature

In order to determine the degree of uranium burnup in a rod, small chips of UO_2 were taken from various radial locations at different points along the length of the rod. The percent of the total original fissionable plus fertile isotopes which had fissioned at a given point was determined by dissolving a portion of the sample from this point out of cell and analyzing the resulting solution for Cs-137 and U or Ce-144 and U. The information from such analyses was then combined with the previously determined gamma scan data to compute the peak and average burnup values for the rod and the total number of atoms (or total weight) of U that had fissioned in a fuel rod. ^(10, 11, 13)

The yields of the different gaseous isotopes from the thermal-neutron fission of U-235 have been experimentally determined. It was thus possible to calculate the amounts of Kr-85, total Kr, and/or total Xe produced in a given rod during its irradiation lifetime. The amount of Kr-85 released, as determined by gamma count, or the amounts of Kr and/or Xe released as determined by chromatography, were divided by the amounts of the respective isotopes generated to obtain the percentage of fission gas released. It was assumed that the percent release for total fission gas would be identical to the percent release for any one of the separate isotopes.

The heat flux at which a given rod operated was calculated from the amount of uranium burned up, the energy produced per fission, the length of time the reactor was at power during the irradiation period, and the rod geometry. Recently acquired data on thermal conductivity were applied to calculate UO_2 centerline temperatures from the heat flux values. (6)

B. IRRADIATION TEST RESULTS

The percent fission gas release determinations for the various rods tested are presented with some of the pertinent design and irradiation exposure data in Table VI. The cross-hatched area of Figure 8 represents the range of fission gas release as a function of fuel temperature for terminal burnup values of approximately 600 to 5000 MWD/ton. Although this correlation resulted in a rather wide scattering of points, the plot does indicate the possibility of 50 to 60 percent of generated fission gases being released between 3500 F and 4000 F. It should be noted that the gas release for all but one of the fuel rods of the element S-II-3-G-P, which had a burnup of only 121 MWD/ton, fell below the general range of values.

Figure 4. Gamma Scan of Element S1-a

TABLE V

SUMMARY OF VBWR OPERATING STATISTICS DURING
IRRADIATION OF FUEL ELEMENT S-II-2-G-P

Run No.	Dates	Maximum Reactor Power (MW)	Average Reactor Power (MW)
	1958		
83	10/22 - 11/6	25	16.8
84	11/21 - 12/7	25	19.1
85	12/9 - 12/22	25	18.6
86	12/24 - 12/29	25	18.2
	1959		
87	1/2 - 1/23	20	19.5
88	1/27 - 2/3	25	18.3
89	2/4 - 2/10	20	19.0
90	2/11 - 2/12	low	4.5
91	2/13 - 2/18	20	16.9
92	2/19 - 2/20	20	6.6
93	2/21 - 2/22	20	13.1
94	2/22 - 2/25	low	9.0
95	3/1 - 3/6	30	24.4
96	3/8 - 3/12	30	21.7

Figure 5. Reactor History, Run #96 (S II 2)

GEAP-4314

Figure 6. PWL-6 Irradiation History, GETR Cycle 9

Figure 7. Fission Gas Puncture Mechanism

TABLE VI

RELEASE OF FISSION GAS FROM APED EXPERIMENTAL UO_2 FUEL

Assembly	Clad Material	Average Burnup for Assembly (MWD/T)	Rod No.	Clad OD (inch)	Clad Wall Thickness (inch)	Pellet Diameter (inch)	Average Axial Heat Flux (Btu/hr-ft ²)*	Average Centerline Temperature (°F)	Fission Gas Release (%)
S-I-1-B-P	304 S.S.	1980	7	0.500	0.036	0.422	134,000	1410	0.31
			14	0.500	0.036	0.422	151,000	1530	0.67
S-II-2-G-P	304 S.S.	1890	C	0.554	0.025	0.497	337,000	3600	41.4
			G	0.554	0.025	0.497	278,000	2760	43.2
			H	0.554	0.025	0.497	265,000	2610	24.0
S-II-3-G-P	304 S.S.	121	A	0.555	0.025	0.500	422,000	4860	14.5
			B	0.555	0.025	0.498	279,000	2970	11.1
			C	0.555	0.025	0.498	297,000	3030	4.0
			D	0.555	0.025	0.500	338,000	3610	8.7
			G	0.555	0.025	0.502	348,000	3780	11.7
			H	0.555	0.025	0.502	315,000	3280	6.3
PWL-6	304 S.S.	600 (Approx)	B	0.427	0.015	0.396	367,000	2990	17.1
			C	0.416	0.010	0.396	180,000	1360	11.8
			D	0.427	0.015	0.396	175,000	1370	4.0
			E	0.426	0.015	0.396	175,000	1360	13.5
DP-1	Zirc-2	3580	B	0.565	0.030	0.498	212,000	2140	15.4
			C	0.565	0.030	0.498	235,000	2410	20.3
			E	0.565	0.030	0.498	245,000	2560	14.3
			G	0.565	0.030	0.498	234,000	2420	11.4
DP-5	Zirc-2	5000	A	0.560	0.030	0.497	284,000	3050	9.16
DP-14	Zirc-2	5250	I	0.560	0.030	0.493	166,000	1630	10.22
NUSU	347 S.S. ⁽¹⁾	815		1.50	0.028	--	280,000	1780	1.58
	Inconel-X ⁽²⁾			1.072	0.025	--			

*Heat flux at outer surface of cladding averaged over length of rod, computed for the periods that the element operated at its maximum power.

(1) Outer cladding of annular fuel element. (2) Inner cladding.

Figure 8. Fission Gas Release as a Function of the Calculated Average Centerline Temperature of UO_2 During Maximum Power Operation

V. DISCUSSION

A. RESIDUAL GAS RELEASE

Outgassing procedures for sintered UO_2 pellets also have been studied as a variable in irradiation experiments conducted in GETR. ⁽¹⁵⁾ From such tests a combination of evacuating and heating to 800 F (427 C), followed by back-filling with helium, was found to be an effective means for outgassing pellet-filled tubular fuel segments. In this study two fuel elements, having annular geometry (cooled both internally and externally) and 3-foot fuel columns, were irradiated at a heat flux of 585,000 Btu/hr-ft² for approximately 5 minutes. In the case of the first element the sintered pellets had been outgassed at 225 F (107 C) in air prior to being loaded in the element, but no additional outgassing was carried out. After irradiation the element was punctured for analysis of the contained gases. The volume of gas collected was approximately four times the volume of helium originally contained in the fuel element. Chromatographic analysis of the collected gas revealed that 35 percent of the gas was methane, 10 percent nitrogen, 13 percent oxygen, 22 percent hydrogen, and the remainder helium.

The second fuel element utilized similar pellets. However, after one end plug was welded in place and the pellets were loaded, the element was outgassed at 800 F in a vacuum and then backfilled with helium. This outgassing and backfilling procedure was repeated twice. The irradiation exposure for this element was the same as that for the first element. Post-irradiation gas collection and analysis revealed that the volume of gases, other than helium, was but approximately one-seventh the quantity of residual gas impurities collected from the first fuel element. The gas analysis indicated that all of the methane and oxygen were now absent, but that nitrogen and hydrogen had not been completely removed by outgassing. Based on the total volume of gas collected (including He), N_2 and H_2 were analyzed as 10 percent each by volume.

The results of the laboratory outgassing experiments of the present study indicated that the residual gas content of arc-fused powder was at least 10 times that of sintered pellets and could be as high as 750 cm³ per kilogram of UO_2 , or nearly 80 times the residual gas content of any of the pellet samples. Hence, including an outgassing step in arc-fused powder fuel fabrication appears particularly desirable.

Improper outgassing of enriched arc-fused UO_2 has resulted in severe hydriding and clad failure of Zircaloy-2 clad fuel elements during irradiation. ⁽¹⁶⁾ Water content in UO_2 can pyrohydrolyze fluoride-containing impurities which are certain to attack the clad interior. At the present time it is not known what threshold value of F^- impurities in UO_2 can be tolerated without sheath failure when moisture is present in UO_2 .

Room temperature evacuation and helium back-filling of arc-fused UO_2 powder was found to be ineffective in expelling absorbed or chemisorbed gaseous impurities. Sintering arc-fused powder at 1650 C in hydrogen was found to be an effective method of removing a major portion of the residual gas, provided the particle size distribution is small and the powder is stored properly prior to loading, or loaded into fuel elements immediately after outgassing.

Experimental evidence presented in this report and data compiled by others show that outgassing rates of arc-fused powder are particle-size, as well as temperature, dependent. (9) For example, in the case of a 4.04 percent U-235 enriched arc-fused powder with a particle size of -3 to +6, the total gases expelled after 30 minutes at 1350 C were 0.025 cc/gm UO_2 . Under the same conditions the same powder, but with a particle size of -6, +20, yielded 0.10 cc and that with a particle size of -20 yielded 0.180 cc/gm UO_2 . Samples of -20 mesh powder were kept standing in air for time intervals varying from a few minutes to 45 days. The gas release increased from 0.2 cc/gm to 0.35 cc/gm after 3 days and to 0.47 cc/gm of UO_2 after 45 days.

Nitrogen impurities in arc-fused UO_2 have been identified as uranium nitride (U_2N_3). Other compounds found by X-ray diffraction techniques included the mono-nitride (UN), mono-carbide (UC), and dicarbide (UC_2). (17) Microscopic examination of arc-fused powder is shown in Figure 9. The needle-like light color regions were identified as UN and U_2N_3 by examining indexing data of their diffraction patterns. X-ray diffraction results are in qualitative agreement with the gas analysis of arc-fused UO_2 powder shown in Table IV. In addition, the expulsion of nitrogen in vacuum at 1200 to 1500 C is in agreement with data reported by Rundle and associates (18) where U_2N_3 was found to break down at 1300 C and UN to decompose slowly at 700 C, both yielding gaseous nitrogen.

Nitrogen impurities in pellets have been reported to enter through a side reaction with uranium carbides, themselves formed when binder residue reacts with uranium dioxide. The end result is a second phase identified as uranium nitride. The mechanism of nitrogen release from sintered pellets involves decomposition of nitrides under vacuum at temperatures up to 1600 C, followed by solid state diffusion through the UO_2 lattice. (19)

In fuel elements where the clad temperatures are 1000 F or higher (as in the case of superheat and gas-cooled reactors), nitriding of the sheath is a possibility, especially when arc-fused UO_2 containing uranium nitrides is used. Effective outgassing for these types of fuel elements is required.

B. FISSION GAS RELEASE

The portion of noble gaseous products of uranium fission that is retained in UO_2 is held in the crystal lattice, grain boundaries, or occluded porosity. The degree of fission gas retention lessens as the temperature rises. Early experimental work, which has been verified by many investigators, indicated that at temperatures up to 1400 C (2550 F) the amount of fission gas released is a direct function of the square root of time. (20)

Actually, the movement of fission gases in UO_2 is probably largely diffusion dependent up to a temperature of about 1650 C (3000 F), which is the approximate point of incipient UO_2 redistribution (movement of UO_2 molecules either to form new crystal boundaries or to sublime). Between 1650 C and 1850 C (3360 F), the mechanism of gas release is transformed to a process of bulk evolution. (21, 22)

Evolution of rare gases from UO_2 at temperatures considerably lower than the melting point is not surprising. A study of the release of gases from metals, by Tucker and Norton, showed considerable gas evolution at temperatures as low as one-third of the way from room temperature to the melting points. (23) Specifically, evolution of krypton from uranium metal foil was found to take place at 300 to 400 C. Maximum evolution of argon from silver was found to be at 500 to 900 C, with twin peaks at 680 and 880 C. On the other hand, argon from gold and lead evolved only at 50 C above their melting points, with negligible rates at or below their melting points. These data suggested that gas mobility varies significantly from one metal to another. Further, krypton in uranium is very mobile, having been evolved well below the alpha to beta transformation temperatures. One possible explanation of differences in mobility of gaseous atoms in metals may be the difference in the density of nucleation sites. Bubble formation would tend to trap gases and bubbles released only when their mobility is enhanced by high temperatures (near or above melting).

In order to achieve high thermal performance of the UO_2 -containing fuel elements, it is presently the practice to design for central temperatures above 1850 C. Because of steep thermal gradients, a considerable portion of the fuel is expected to operate above 1650 C where gas diffusion in solid state begins to give way to gas release by other means. Under these conditions it has been found that fission gas release is appreciable. (1)

Typical cross sections of fuel rods after irradiation are shown in Figure 10. Void formation is an indication that uranium dioxide rearrangement has taken place, possibly through grain growth, sublimation, or both. Columnar grains shown in Figure 11 were taken at the edge of the voids shown in Figure 10.

According to the consensus of experimenters, columnar grains can form, at temperatures as low as 1500 C in some cases, by the process of sublimation-vapor deposition. Laboratory experiments show that at temperatures as low as 1800 C, UO_2 may deposit out in dendritic form. (21) Porosity observed at the grain boundaries nearest the central void have been postulated to be "frozen-out" evidence of a vaporization-deposition process. (22) Gases are expected to move toward the central void and be released by this process. The movement of these voids by this sublimation-deposition process is expected to be slower at the root of the columnar region and rapid near the central void. Because of its complexity, the mechanism of fission gas evolution at temperatures above the redistribution range has not lent itself to a satisfactory theoretical formulation.

However, reactor experiments with large-size test fuel elements are a reasonably reliable means of determining fission gas release, and can be used in design calculations. Grouping of the data obtained from the VBWR and GETR experiments is reasonable in view of the similarities in fuel rod design and in the density, stoichiometry, and general preparation of UO_2 pellets. The secondary nature of the effect of uranium burnup level has been demonstrated elsewhere. (5)

Despite these similarities, Figure 8 shows a wide spread in the data. Even when large size fuel elements are used, the accumulation of possible errors in these experiments is great. Gas collection and analysis may introduce large errors, not merely because of the size of the samples to be analyzed but also due to analytical techniques available. The branching ratio of Kr-85 isotope was in doubt a few years ago. (14) Cerium and cesium isotopic analyses, upon which the maximum burnup depends, are beset by possible errors in actual decay half lives, (24) and by migration of these species upon UO_2 redistribution during these high temperature irradiation experiments. Furthermore, existing laboratory standard solutions for Cs-137 are associated with certain error, to say nothing of the analytical procedures themselves used in each sample. In plots where fission gas release is attempted to be related to temperature of UO_2 , additional calculational errors may be introduced. Thermal conductivity of UO_2 , contact conductance at the UO_2 -clad interface, and film coefficients at the metal-coolant surfaces are quantities that are still not too well defined.

For the purpose of comparison, the results of experiments carried out by Bettis Atomic Power Laboratory (25, 26) and Oak Ridge National Laboratory (27, 28) are shown in Figure 12 along with the APED data band, taken from Figure 8. One possible reason the APED data is located to the left of and above the data reported on experiments with UO_2 pellets by ORNL and by other investigators is the fact that the APED data are plotted as a function of average fuel element temperature. ORNL data were obtained by actually measuring UO_2 temperatures during outgassing in the laboratory. (28) For fuel elements where a steep temperature gradient exists across the cylindrical cross section, pin-pointing temperature regions and assigning fission gas release for each region would be subject to question as to its accuracy. Fission gas collected in the plenum has accumulated from all temperature regions; therefore, the plot with average temperature as an abscissa is a logical choice.

Another consideration is the relative lengths of irradiation time. If one assumes that the appearance of voids at the grain boundaries can be interpreted in terms of a vaporization-deposition process, as discussed previously, one would expect fission gas release from the columnar grain region to be time dependent. A 5-hour irradiation time was employed in the laboratory heating experiments on pellets at ORNL. (28) The location of these data points relative to the APED band may be due at least in part, to a time lag for the void migration across the columnar grains. This same factor also may be the reason for the relatively low fission gas releases for the S-II-3-G-P fuel rods (Figure 8). This element was irradiated for a period considerably shorter than the exposure times for the other APED assemblies.

Internal fuel element pressure buildup has been measured in "situ" as a function of irradiation exposure in the VBWR. ⁽³⁾ Measurements were made in fuel elements equipped with pressure transducers. Data indicated that pressure buildup was a function of both reactor power (hence UO_2 temperature) as well as accumulated exposure. For fuel elements operating at an estimated average temperature of 2370 F (1300 C), the fission gas release was found to be 50 percent the theoretical yield of fission gas.

Fission gas release values either from arc-fused powder compacts or compacts which were swaged have not as yet been available in quantities comparable to those available from sintered pellet fuel elements. Fragmentary information from early Hanford experiments is inconclusive. ⁽²⁹⁾ Early experimental results have been included in Table VII. It has been postulated that sintering of the powder compacts observed in irradiation tests will result in fission gas release similar to that observed in sintered pellets. Lower temperature regions in fuel elements containing powder are likely to release more fission gases than comparable regions in pellets*. Experiments now in progress are expected to provide the required data for compacted powder fission gas release.

TABLE VII

FISSION GAS RELEASE

Comparison of Pellets and Powder Compacted Fuel Elements

Method	Fuel Element Diameter (inch)	Exposure MWD/T	Heat Flux Btu/hr-ft^2	Fission Gas Release Percent
Arc-fused, Vibratory Compacted	0.510	900	250,000	2
Arc-fused, Swaged	0.520	750	210,000	6
Sintered Pellets	0.500	750	210,000	1
Sintered, crushed, then Swaged UO_2	0.625	1,500	450,000	45
Hanford Atomic Products Operation, "Novel Ceramic Fuel Fabrication Processes USAEC Report, HW-64629, April 15, 1960.				

*Standard UO_2 pellets for reference are 94 percent of theoretical density with O/U ~2.00.

Figure 9. Uranium Nitride Inclusions of Arc-fused UO_2 Powder, in the as Received Condition. 500X

Figure 10. Progressive Stages of Recrystallization Along the Axial Length of a Typical Fuel Element From S-II-2-G-P. Cross Section Showing Void Originated From Peak Heat Flux Region Operated at 380,000 Btu/ft²-hr. Center Photograph at Heat Flux Region of 330,000 Btu/ft²-hr. Initial Diametrical UO₂ Clad Gap was 0.013 Inches.

GEAP-4314

Rod C 14 Inches from Top of Rod

Rod C 6 Inches from Top of Rod

Rod D 14 Inches from Top of Rod

Axis

B

Figure 11. SAVANNAH II - 2 MICROPHOTOS 80X

Figure 11. SAVANNAH II - 2 MICROPHOTOS 80X

Figure 12. Fission Gas Release Versus UO₂ Temperature From BETTIS and ORNL Experiments

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