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**Irradiation Performance of HTGR Fertile Fuel
in HFIR Target Capsules HT-12 through HT-15:
Part I—Experiment Description and
Fission Product Behavior**

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OAK RIDGE NATIONAL LABORATORY

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METALS AND CERAMICS DIVISION

Base Technology Program
Fuel Graphite Development (189aO1330)

IRRADIATION PERFORMANCE OF HTGR FERTILE FUEL
IN HFIR TARGET CAPSULES HT-12 THROUGH HT-15:
PART I – EXPERIMENT DESCRIPTION AND FISSION PRODUCT BEHAVIOR

M. J. Kania M. T. Morgan
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IRRADIATION PERFORMANCE OF HTGR FERTILE FUEL IN HFIR TARGET CAPSULES HT-12 THROUGH HT-15: PART I—EXPERIMENT DESCRIPTION AND FISSION PRODUCT BEHAVIOR

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ABSTRACT

Sixteen types of Bisco-coated designs, on ThO₂ kernels, were irradiated in High Flux Isotope Reactor target capsules HT-12 through HT-15. This report addresses the description of the experiment and extensive postirradiation analyses and experiments to determine fertile-particle burnup, fuel coating failures, and fission product behavior. Several low-temperature isotropic (LTI) pyrocarbon coatings, which "survived" according to visual inspection, were shown to have developed permeability during irradiation. These particles were irradiated at temperatures $\approx 1250^\circ\text{C}$ and to burnups $\geq 8\%$ fission per initial heavy-metal atom (FIMA). No evidence of permeability was found in similar particles irradiated at temperatures $\approx 1550^\circ\text{C}$ and burnups $\approx 16\%$ FIMA. Failures due to permeability were not detectable by visual inspection but required a more extensive investigation by the 1000°C gaseous chlorine leaching technique.

Maximum particle surface operating temperatures were found to be approximately 300°C in excess of design limits of 900°C (low-temperature magazines) and 1250°C (high-temperature magazines). The extremes of high temperatures and fast neutron fluences up to 1.6×10^{22} neutrons/cm² produced severe degradation and swelling of the Poco[†] graphite magazines and sample holders.

The amount of krypton + xenon released into the void space in the kernels of intact ThO₂ particles was found to be primarily burnup dependent and reached about 90% at design burnup. Oxygen release per fission was found to be a function of temperature and burnup with the empirical expression $O/f = (a + bf) \exp(-Q/RT)$ representing data from ThO₂ particles irradiated in the target facility and stored out-of-reactor for about two years. The oxygen release was significantly affected by the interaction of urania with sesquioxides of yttrium plus rare-earth elements. The irradiated particles showed complete retention of fission products ¹⁰⁶Ru and ¹⁴⁴Ce at the extremes of temperature and burnup, whereas ¹³⁷Cs and ¹²⁵Sb were lost under the same conditions. Cesium loss was 20 to 40% for burnups of 6 to 16% FIMA in the impermeable coatings and about 65% in particles with defective coatings at the higher temperatures. Cesium loss at the lower temperatures and burnups was $< 1\%$. Cesium diffusion coefficients in the bare kernels of the same coated particles ranged from 1×10^{-17} to 2×10^{-15} cm²/sec, increasing with burnup.

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†Grade AFX-5Q manufactured by Poco Graphite Inc., a subsidiary of Union Oil Company, Decatur, Texas.

1. INTRODUCTION

An initial phase in the program of accelerated irradiation experiments is the loose-coated particle tests conducted in the target facility¹ of the High Flux Isotope Reactor.² These experiments, commonly known as the HT-series, screen various coated particle designs and fuel rod matrix designs at, or in excess of, temperatures and fast neutron fluences accumulated in a commercial HTGR. Because of the high neutron fluxes in the target region, full fluences of 8×10^{21} neutrons/cm² ($E > 0.18$ MeV) can be achieved in three to four months as compared with the required six years in an HTGR.

This experiment was made up of four target capsules designated HT-12, -13, -14, and -15. It was designed to test a series of 16 batches of Bisco-coated ThO₂ particles at peak temperatures of 900 and 1250°C, to burnup and fast neutron exposures up to twice the HTGR design requirements. Nine of these batches were coated by Oak Ridge National Laboratory, and the remaining seven by General Atomic Company.³ The ORNL-designed coatings were selected with the use of the STRETCH⁴ computer code so that some particles would fail while others survived. The capsules were irradiated for two, four, six, and seven HFIR cycles respectively.

The primary objectives of this experiment were:

1. to test selected Bisco-coated ThO₂ particles at conditions that would induce predictable particle failure and thereby establish minimal coating engineering design criteria;
2. to determine numerical values for material constants (as far as possible) required in the stress analysis code, STRETCH.

In addition, several selected batches of particles were extensively investigated to determine: (1) burnup, cesium retention by the particle, and internal gas pressures; (2) failure and fission product release in Bisco-coated ThO₂ particles; (3) pyrocarbon coating characterization.

Minimal coating engineering design criteria for Bisco-coated ThO₂ particles were not established in this experiment. This was due to the inability to examine all irradiated coating batches with experimental techniques necessary to establish, with certainty, failed particles in each batch. Because of the uncertainty, both in failure determination and in the cause of failure, it was not possible to correlate the predicted results, using the STRETCH code, with the experimental results. Thus, no results are reported for the material constants required in the STRETCH code. The results of work in progress to determine coating integrity and to correlate the STRETCH model analysis to experimental data will be reported in TM-5306.

References

1. B. H. Montgomery, "Irradiation Tests in the HFIR Target Facility," *Gas-Cooled Reactor Programs Ann. Prog. Rep. Dec. 31, 1972*, ORNL-4911, pp. 113-15.
2. R. D. Cheverton and T. M. Sims, *HFIR Core Nuclear Design*, ORNL-4621 (July 1971).
3. *HTGR Fuels and Core Development Program*; *Q. Prog. Rep. Aug. 30, 1974*, GA-A13126, pp. 52-74.
4. J. W. Prados and T. G. Godfrey, *STRETCH—A Computer Program for Predicting Coated-Particle Irradiation Behavior; Modification IV, December 1967*, ORNL/TM-2127 (April 1968).

2. DESCRIPTION OF CAPSULES HT-12 THROUGH HT-15

This experiment consisted of four target capsules designated HT-12, -13, -14, and -15. Each capsule contained four tapered graphite magazines each supporting coated particle samples in small graphite crucibles. Two of the magazines were designed for a graphite crucible surface temperature of 1250°C, and the remaining two for a temperature of 900°C. The four capsules were designed for two, four, six, and eight HFIR cycles to achieve a fast neutron exposure from 2×10^{21} to 18×10^{21} neutrons/cm² ($E > 0.18$ MeV). Burnup in the ThO₂ would range from 2 to 20% FIMA.

The design of an HT capsule used in loose-coated particle experiments is illustrated in Fig. 2.1. The active test space is a right circular cylinder approximately 0.51 m (20.0 in.) long by 13.46 mm (0.53 in.) in diameter centered about the reactor horizontal midplane (HMP). Each capsule contained 52 Poco graphite cylindrical sample holders of nominal dimensions 6.985 mm (0.275 in.) long by 9.779 mm (0.385 in.) in diameter. Thirty-two contained Biso-coated ThO₂ particles, and the remaining 20 contained low-enriched (7%) uranium particles. The uranium particles were included as the initial heat source and to flatten axial temperature distribution. Thirteen sample holders, each separated by a 0.0127-mm-thick (0.0005-in.) zirconium foil, were loaded into each of four tapered Poco graphite magazines—eight containing ThO₂ particles and five containing uranium particles. End plugs were placed in the top and bottom of each magazine, with those nearest to the HMP being loaded with uranium particles. Figure 2.2 shows the Poco graphite particle sample holder and magazine. A total of 16 fertile-particle sample holders were irradiated in the high-temperature, high-flux regions nearest the HMP, and 16 were irradiated in the low-temperature, low-flux regions located near the ends of the capsule. The four completed magazines were then placed in an aluminum primary containment vessel 13.030 mm (0.513 in.) in inside diameter by 16.137 mm (0.655 in.) in outside diameter. With the upper and bottom caps attached, the overall length of the capsule was 0.9 m (35.0 in.). Each capsule was evacuated and baked-out at 300°C for 4 hr, backfilled with argon, and sealed.

2.1 Fuel

2.1.1 Coated Particle Design

The fertile particle makes up 80% or more of the coated particle volume in current fuel rod designs for HTGRs. The fertile particle design consists of two-layer (Biso) coatings primarily for economic reasons. The particle configuration for the Biso-coating design consists of a fuel kernel successively coated with a low-density buffer layer and a high-density isotropic carbon layer (LTI). Important variables in the coating design, which are necessary to maintain fuel particle integrity, are the total thickness of the coating layers, thickness ratios, the creep coefficient, and the outer pyrocarbon anisotropy.

To meet the objectives of this experiment, it was necessary to design particle coatings so that some would fail and others survive. It was also necessary to be able to examine the particles after selected intervals of accrued fast fluence ($E > 0.18$ MeV). The reference particle design¹ for this experiment was a 500-μm-diam ThO₂ kernel and a Biso coating consisting of an 85-μm-thick buffer layer and a 75-μm-thick outer isotropic carbon layer. This same fertile particle design is currently specified for initial and recycle HTGR fuel.

Variations on the reference coating design were selected for testing on the basis of irradiation performance predicted by the STRETCH computer code. The two most sensitive physical variables used in the code were the creep coefficient and the outer carbon layer anisotropy.

Fig. 2.1. Target capsule typical of HT-12, -13, -14, and -15.

Fig. 2.2. Graphite sample holder and magazine for capsules HT-12 through HT-15.

Biso-coating designs were calculated using nominal neutron flux and temperature values. A creep coefficient of 10^{-27} in./in.-psi-neutrons/cm² was assumed for the calculations, and the effect of variations by a factor of 5 were studied. The Bacon anisotropy factor was assumed to be 1.05, but values of 1.00 to 1.15 were also used in the calculations. A value for the densification constant equal to 0.046 per 10^{20} neutrons was used in all of the calculations. A failure criteria of 20,000 psi of tangential stress on the outer LTI was assumed for each design. Within these parameters the particles were predicted to fail at the rate of two types for each irradiation cycle in the HFIR.

2.1.2 Preparation of Test Samples

The ThO₂ kernels for the experiment were screened from a large batch of sol-gel-derived² microspheres so that the diameter distribution of each kernel batch would have a standard deviation ≤ 7 μ m. Both 400- and 500- μ m-diam kernels were used. A total of 16 particle batches were prepared. Nine of these were coated by ORNL, and the remaining seven by General Atomic. All of the ORNL particle batches were coated in a 25.4-mm-diam (1.0-in.) coating furnace. The buffer layers were deposited at 1200°C, using a coating gas composition of 75% C₂H₂ and 25% helium. The outer LTI coatings were deposited at 1400°C, using a coating gas concentration of 75% C₃H₆ and 25% helium. Deposition rates for each ORNL coating along with the characterization of each particle batch are described in Table 2.1. All ORNL particle batches were annealed at 1800°C in an argon environment for 30 minutes prior to irradiation.

2.2 Loading Scheme for Capsules

As previously described, each capsule was identical and contained 52 sample holders: 32 filled with ThO₂ particles and 20 filled with uranium particles. The 16 types of particles were distributed as indicated in Table 2.2 such that each of the four magazines would contain eight ThO₂ particle holders and five uranium holders. This allowed each particle batch to be irradiated in one position in each of the high- and low-temperature regions. The number of ThO₂ particles irradiated was 75 per sample holder in

Table 2.1. Coating deposition rates and characterization of coated particles in capsules HT-12 through HT-15

Batch	Deposition rate ^a ($\mu\text{m}/\text{min}$)		Kernel diameter ^b (μm)	Buffer		LTI		OPTAF ^e
	Buffer	LTI		Thickness ^b (μm)	Density ^{c,d} (g/cm^3)	Thickness ^b (μm)	Gradient density (g/cm^3)	
OR-1749	32.4	24	402 $\pm$ 3.04	32.9 $\pm$ 7.7	1.1	36.4 $\pm$ 3.2	1.92	1.03 ^f
OR-1826	31.9	20.4	402 $\pm$ 3.04	21.4 $\pm$ 3.3	1.1	30.6 $\pm$ 3.89	2.01	<i>g</i>
OR-1830	ND ^h	19.8	402 $\pm$ 3.04	1 $\pm$ ND ^h	1.1	38.1 $\pm$ 4.56	2.01	<i>g</i>
OR-1837	ND ^h	20.7	402 $\pm$ 3.04	1 $\pm$ ND ^h	1.1	24.4 $\pm$ 2.8	2.02	<i>f,g</i>
OR-1838	37.0	20.1	402 $\pm$ 3.04	32.3 $\pm$ 3.9	1.1	63.8 $\pm$ 4.1	1.96	1.02 ^f
OR-1840	57.0	19.4	402 $\pm$ 3.04	24.6 $\pm$ 3.4	1.1	50.1 $\pm$ 4.3	2.01	<i>g</i>
OR-1846	50.0	21.2	402 $\pm$ 3.04	20.3 $\pm$ 3.2	1.1	21.2 $\pm$ 2.29	1.99	<i>g</i>
OR-1849	56.0	21.4	508 $\pm$ 1.66	79.4 $\pm$ 6.7	1.1	74.7 $\pm$ 4.3	1.99	1.02 ^f
OR-1850	72.0	19.9	508 $\pm$ 1.66	44.5 $\pm$ 5.6	1.1	48.1 $\pm$ 3.5	1.99	<i>g</i>
4252-00			405 $\pm$ 9.0	81.0 $\pm$ 6.1	1.26	76.0 $\pm$ 5.9	2.00	1.14
4252-01			487 $\pm$ 14.7	61.0 $\pm$ 7.4	1.11	76.0 $\pm$ 8.3	2.02	1.16
4252-02			508 $\pm$ 9.6	83.0 $\pm$ 6.9	1.08	75.0 $\pm$ 7.5	1.84	1.07
4252-03			501 $\pm$ 14.3	92.0 $\pm$ 9.8	1.08	67.0 $\pm$ 5.6	2.00	<i>i</i>
4252-06			514 $\pm$ 8.7	80.0 $\pm$ 6.3	1.10	74.0 $\pm$ 6.0	1.82	1.14
4252-07			485 $\pm$ 22.4	46.0 $\pm$ 4.5	1.03	50.0 $\pm$ 4.1	1.96 ^j	1.20
4252-08			499 $\pm$ 16.5	39.0 $\pm$ 6.2	1.08	119.0 $\pm$ 11.1	1.95	1.14

^aDeposition rates are quoted for ORNL particles only.

^bMean value $\pm$ standard deviation.

^cDensity values for ORNL particles are design values.

^dGeneral Atomic density measurements made on parent particle batch or calculated.

^eOPTAF values obtained from procedure described in D. W. Stevens, "Optical Anisotropy in Nearly Isotropic Pyrolytic Carbons," pp. 167–68 in *11th Biennial Conference on Carbon*, June 4–8, 1973, CONF-730601, Sponsored by the American Carbon Committee and Oak Ridge National Laboratory.

^fORNL OPTAF measurements described in Sect. 10.1.

^gThe design OPTAF for ORNL outer PyC coatings of <1.1 was used.

^hND = not determined.

ⁱOPTAF value for this batch was >1.5 , and the maximum measurable OPTAF is 1.5.

^jThe buffer and OPyC layers could not be separated from split samples sent for density determinations. The value shown was determined from a grab sample taken after coating.

the high-temperature, high-fluence regions, and 53 in the low-temperature, low-fluence regions. The two high-temperature regions each contained 0.265 g of thorium and 0.134 g of uranium. The two low-temperature regions each contained 0.1875 g of thorium and 0.0955 g of uranium. The total weight per capsule of thorium was 0.905 g, and per capsule of 7% enriched uranium was 0.459 g. Each uranium holder and end cap contained 22.34 mg of uranium in the high-temperature regions and 15.0 mg in the low-temperature regions.

Table 2.2. Loading scheme for capsules HT-12, -13, -14, and -15

Sample holder		Batch number	Design ^a	Case number	Particle type
Low temperature	High temperature				
1	14				U
2	15	4252-08	499-39-119	1	ThO ₂
3	16				U
4	17	OR-1850	508-45-48	2	ThO ₂
5	18	OR-1846	400-20-21	3	ThO ₂
6	19				U
7	20	4252-00	405-81-76	4	ThO ₂
8	21	OR-1840	402-25-50	5	ThO ₂
9	22				U
10	23	4252-06	514-80-74	6	ThO ₂
11	24	OR-1749	402-33-36	7	ThO ₂
12	25				U
13	26	OR-1849	508-79-75	8	ThO ₂
40	27	4252-02	508-83-75	9	ThO ₂
41	28				U
42	29	OR-1838	402-32-64	10	ThO ₂
43	30	4252-03	501-92-67	11	ThO ₂
44	31				U
45	32	OR-1826	402-21-31	12	ThO ₂
46	33	4252-01	487-61-76	13	ThO ₂
47	34				U
48	35	OR-1830	402-1-38	14	ThO ₂
49	36	4252-07	485-46-50	15	ThO ₂
50	37				U
51	38	OR-1837	402-1-24	16	ThO ₂
52	39				U

^aDesign dimensions given as mean kernel diameter, mean buffer thickness, and mean PyC thickness.

References

1. Oak Ridge National Laboratory, Gulf General Atomic, and Allied Chemical Corporation, *National HTGR Fuel Recycle Development Program Plan*, ORNL-4702 (rev. 1, draft) (August 1973).
2. P. A. Haas, *Sol-Gel Preparation of Spheres: Design and Operation of Fluidized Bed Columns*, ORNL-4398 (September 1969).

3. IRRADIATION OF CAPSULES HT-12 THROUGH HT-15

3.1 Description of Facility

The experimental capsules HT-12 through HT-15 were irradiated in the target facility of the HFIR. This facility is located in the center of the two concentric fuel annuli of the reactor core. Figure 3.1 describes the location of this region, which contains 30 target positions, three of which were used for the HT capsules and the remaining 27 for transuranium element production. Figure 3.2 describes the time variation of the thermal ($E < 1.86$ eV) and the fast (nonthermal) ($E > 1.86$ eV) group neutron fluxes¹ during a typical HFIR cycle of 23 days. The nominal peak thermal flux at the reactor HMP for day 0 was 2.81×10^{15} neutrons $\text{cm}^{-2} \text{sec}^{-1}$, and the nominal peak fast (nonthermal) flux was 3.09×10^{15} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. These fluxes remained relatively constant during the cycle, deviating somewhat less than 4% over the entire cycle at reactor full power of 100 MW. The axial variation of the neutron fluxes² is shown in Fig. 3.3 as a function of distance from the HMP. At a distance of 0.25 m (10.0 in.) from the midplane,

Fig. 3.1. HFIR cross section at horizontal midplane.

Fig 3 2 Nominal thermal and nonthermal fluxes applicable to the HMP of the target facility of the HFIR during one reactor cycle

Fig 3 3 Nominal HFIR target neutron fluxes and gamma heating rate

corresponding to the ends of the capsules, the flux values have decreased by a factor of 2. Both the thermal and fast (nonthermal) fluxes are considered symmetric about the HMP.

Also shown in Fig. 3.3 are the axial variation in the fast neutron flux ($E > 0.18$ MeV) and the gamma heating rate as a function of distance from the reactor HMP. The peak value for the fast neutron flux ($E > 0.18$ MeV) at the midplane is 1.17×10^{15} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. Eighty percent of the heat generated within an HT capsule is due to gamma heating.³ The maximum and minimum values for the high-temperature sleeves are 33.5 and 29.4 W/g, respectively, and for the low-temperature sleeves 26.3 and 20.4 W/g respectively.

3.2 Operational History⁴

Target capsule HT-12 was inserted in target position F-3 on September 10, 1972, and was removed on October 23, 1972, after 38.62 days at 100 MW reactor power. The peak fast fluence was 3.9×10^{21} neutrons/ cm^2 ($E > 0.18$ MeV), and peak fertile particle burnup was 1.92% FIMA.

Capsule HT-13 was inserted in target position G-6 on October 8, 1972, and was removed on January 10, 1973, after 85.58 days at 100 MW reactor power. Peak fast fluence was 8.6×10^{21} neutrons/ cm^2 ($E > 0.18$ MeV), and peak fertile particle burnup was 8.43% FIMA.

Capsule HT-14 was inserted in target position F-3 on November 20, 1972, and was removed on April 15, 1973, after 137.00 days at 100 MW reactor power. The peak fast fluence was 1.4×10^{22} neutrons/ cm^2 ($E > 0.18$ MeV), and the established peak fertile particle burnup was 16.6% FIMA.

Table 3.1. Irradiation history

HFIR cycle	Begin	End	Time interval (days)	Power (MW)	Accumulated irradiation (100-MW power days)			
					Capsule			
					HT-12	HT-13	HT-14	HT-15
82	9-10-72	10-3-72	23.44	100	23.44			
Down			5.00	0				
83	10-8-72	10-23-72	15.18	100	38.62	15.18		
Down			1.00	0				
84a	10-24-72	11-11-72	18.00	100		33.18		
Down			2.00	0				
84b	11-13-72	11-19-72	5.37	100		38.55		
Down			1.00	0				
85	11-20-72	12-13-72	23.09	100		61.64	23.09	23.09
Down			0.50	0				
86	12-13-72	12-22-72	8.51	100		70.64	32.09	32.09
86	12-22-72	12-23-72	1.00	83		71.47	32.92	32.92
86	12-23-72	12-25-72	2.00	50		72.47	33.92	33.92
86	12-25-72	1-7-73	13.00	100		84.98	46.35	46.35
Down			2.00	0				
87a	1-9-73	1-10-73	0.60	100		85.58	46.95	46.95
Down			2.10	0				
87b	1-12-73	2-3-73	21.75	100			68.70	68.70
Down			0.40	0				
88	2-3-73	2-26-73	22.71	100			91.41	91.41
Down			1.00	0				
89	2-27-73	3-22-73	22.73	100			114.14	114.14
Down			1.00	0				
90	3-23-73	4-15-73	22.86	100			137.00	137.00
Down			3.00	0				
91	4-18-73	5-11-73	22.96	100				159.96

Capsule HT-15 was inserted in target position A-2 on November 20, 1972, and was removed on May 11, 1973, after 159.96 days at 100 MW reactor power. The peak fast fluence was 1.6×10^{22} neutrons/cm² ($E > 0.18$ MeV), and the estimated peak fertile particle burnup was 20.3% FIMA.

Table 3.1 describes the operation history of the reactor during the irradiation of each capsule. Table 3.2 summarizes the thermal and fast neutron fluxes, fast neutron fluence ($E > 0.18$ MeV), and the estimated fertile particle burnup for each sample holder in each capsule. No attempt has been made to estimate the fissile particle burnup.

Table 3.2. Irradiation summary for capsules HT-12 through HT-15

Sample holder	Distance from specimen holder to HMP ^a (in)	Thermal ^b flux	Fast ^c flux	Fast ^d flux	Ratio, fast/thermal		Fast neutron fluence (E > 0.18 MeV, neutrons/cm ² × 10 ²¹)				
					c/b	d/b	HT-12	HT-13	HT-14	HT-15	
Low Temperature											
2 51	8 909	1 75	1 41	0 59	0 81	0 42	2 0	4 3	6 9	8 1	
4 49	8 344	1 87	1 57	0 67	0 84	0 43	2 2	4 9	7 9	9 3	
5 48	8 061	1 93	1 67	0 70	0 87	0 42	2 3	5 2	8 3	9 7	
7 46	7 496	2 05	1 85	0 76	0 90	0 41	2 5	5 6	9 0	10 5	
8 45	7 214	2 11	1 92	0 80	0 91	0 42	2 6	5 8	9 4	11 0	
10 43	6 649	2 24	2 08	0 85	0 93	0 41	2 8	6 2	10 0	11 7	
11 42	6 366	2 31	2 16	0 88	0 94	0 41	2 9	6 5	10 4	12.2	
13 40	5 801	2 42	2 30	0 93	0 95	0 40	3 0	6 7	11 0	12.8	
High Temperature											
15 38	3 909	2 83	2 70	1 06	0 95	0 39	3 5	7 8	12 5	14 6	
17 36	3 344	2 94	2 80	1 09	0 95	0 39	3 6	8 1	12 9	15.1	
18 35	3 061	3 00	2 83	1 11	0.94	0 39	3 7	8 2	13 1	15.3	
20 33	2 496	3 10	2 91	1 13	0 94	0 39	3 8	8 3	13 4	15 6	
21 32	2 214	3 13	2 94	1 14	0 94	0 39	3 8	8 4	13 5	15 7	
23 30	1 649	3 19	3 00	1 16	0 94	0 39	3 9	8 5	13 7	16.0	
24 29	1 366	3 22	3 03	1 16	0 94	0 38	3 9	8 6	13 8	16 1	
26 27	0 801	3 25	3 11	1 17	0 96	0 38	3 9	8 6	13 9	16 2	

^aHMP = horizontal midplane

^bNeutrons cm⁻² sec⁻¹ ($E < 1.86$ eV $\times 10^{-15}$)

^cNeutrons cm⁻² sec⁻¹ ($E > 1.86$ eV $\times 10^{-15}$)

^dNeutrons cm⁻² sec⁻¹ ($E > 0.18$ MeV $\times 10^{-15}$)

References

1. R. D. Cheverton and T. M. Sims, *HFIR Core Nuclear Design*, ORNL-4621, p. 26 (July 1971)
2. Unpublished work of J. D. Jenkins.
3. Personal communication, P. H. Montgomery to M. J. Kania, August 1974.
4. B. H. Montgomery, "Irradiation Tests in the HFIR Target Facility," *Gas-Cooled Reactor Programs Ann. Prog. Rep. Dec. 31, 1973*, ORNL-4975, pp. 128-30.

4. CAPSULE DISASSEMBLY

4.1 Visual Inspection^{1,2}

Each of the capsules was opened by cutting off the ends of the aluminum containment tube. In capsules HT-12 and -13, the high- and low-temperature magazines were easily removed. In capsule HT-14, some difficulties were encountered in removing the high-temperature magazines because of the swelling of the Poco graphite. In capsule HT-15 the swelling of the Poco graphite magazine had completely closed the initial gap between it and the containment tube. Magazines were removed only after slitting the aluminum containment.

Individual particle sample holders were then pushed out of the graphite magazines into a tray, and the contents of each were visually inspected. Some difficulties were experienced in retrieving the samples in the high-temperature holders in HT-13, -14, and -15 because of the degradation and swelling of the Poco graphite (sample holders). The results of the visual inspection and the stereoscopic examination of particles in each sample holder for each capsule are described below.

HT-12

Capsule HT-12 was observed to be free of the sooty material previously found in most target capsules. This was attributed to the gettering action of the zirconium foil disks placed between the specimen holders in the magazines; however, some sticking of the specimen holders to each other was observed. No evidence of pitting or corrosion on the graphite magazine was observed.

ORNL particles. No failures were observed for particles irradiated in the low-temperature sample holders as determined by visual inspection. In the high-temperature sample holders, one particle batch, OR-1837, experienced a 55% failure rate (41 out of 75).

GAC particles. In the low-temperature holders, one particle batch, GGA 4252-06, experienced a 2% failure rate (1 out of 53). Of the samples irradiated in the high-temperature holders, only two performed without any observed failures, batches GGA 4252-06 and GGA 4252-02. All of the other five samples experienced a high fraction of failed coatings. All GAC samples were shipped to San Diego for further examination and evaluation.³

HT-13

The capsules and magazines were observed to be free of soot as in the previous capsule. However, an important observation from this examination was the degradation and swelling of the Poco graphite sample holders irradiated in the high-temperature regions. Even though there was no evidence of oxidation or mass transport in the sealed capsule, the graphite was so weak and friable that the sample holder screw caps could not be removed without drilling out the threads.

ORNL particles. In the low-temperature sample holders, all samples except batch OR-1749 survived. This sample had an intermediate coating design and experienced a 13% failure rate (7 out of 53). In the high-temperature holders, four samples with thin coatings—batches OR-1846, -1826, -1830, and -1837—showed complete or a high incidence of failure, whereas similar samples with conservatively designed coatings survived. One sample (proposed reference), batch OR-1849, with a 500- μ m-diam kernel survived completely, whereas a similar sample, OR-1850, with a thinner coating failed almost completely.

GAC particles. In the low-temperature holders, only two samples, batches GGA 4252-06 and GGA 4252-02, survived completely, whereas all the others showed a significantly high rate of failure. In the

high-temperature holders, all samples showed complete or high rate of failure. All GAC samples were shipped to San Diego for further examination and evaluation.³

HT-14

The capsules and magazines were relatively free of soot and did not show any evidence of corrosion. The two low-temperature magazines were unloaded without difficulty, and the samples of coated particles were easily removed. However, the two magazines and associated graphite sample holders in the high-temperature regions exhibited extreme swelling.

ORNL particles. In the low-temperature holders, samples from batch OR-1846 had a 2% failure rate (1 out of 53), batches OR-1850 and OR-1749 each had a 4% failure rate (2 out of 53), and batch OR-1826 had a 19% failure rate (10 out of 53). The remaining samples performed without any observed failures. In the high-temperature holders, all but three samples failed completely or had high failure rates. Batches OR-1840 and OR-1849 survived completely, and batch OR-1838 had a 3% failure rate (2 out of 75).

GAC particles. All the samples except two, batches GGA 4252-06 and GGA 4252-02, showed a complete or high rate of failure in the low-temperature holders. All of the samples in the high-temperature holders failed completely or showed a high rate of failure. All of GAC's samples were shipped to San Diego for further inspection and evaluation.³

HT-15

Capsule HT-15 was withdrawn after a seven-cycle irradiation because of the extreme swelling of the Poco graphite holders and magazines observed in HT-14.

ORNL particles. In the low-temperature holders, four samples had survived completely. For the remaining samples, failure rates were: 4% for batch OR-1830 (2 out of 53), 6% for batch OR-1850 (3 out of 53); 9% for batch OR-1837 (5 out of 53), 13% for batch OR-1749 (7 out of 53), and 21% for batch OR-1826 (11 out of 53). In the high-temperature holders, two samples survived completely, batches OR-1749 and OR-1838. The proposed reference design, batch OR-1849, had a 3% failure rate (2 out of 75). The remaining samples showed a complete or high rate of failure.

GAC particles. One sample, GGA 4252-06, survived completely, whereas all others showed a complete or high rate of failure in the low-temperature holders. All of the samples in the high-temperature holders exhibited complete failure. All GAC samples were shipped to San Diego for further examination and evaluation of results.³

Table 4.1 summarizes the results from the visual inspection of the samples irradiated in capsules HT-12 through HT-15.

4.2 Graphite Dimensional Changes

As noted earlier, diametrical expansion of the Poco graphite magazines was severe in the high-temperature regions of capsules HT-14 and -15. In HT-14, the extreme swelling nearly closed the gap between the magazine and the aluminum containment tube. For this reason, capsule HT-15 was withdrawn from the reactor one cycle ahead of schedule. Examination of capsule HT-15 showed that the extreme swelling of the graphite magazines in the high-temperature regions had completely closed the initial gap between it and the aluminum tube. Based on design dimensions, the diametrical expansion of the high-temperature magazines in capsule HT-15 was more than 6%. Table 4.2 describes the graphite dimensional changes observed for the high- and low-temperature magazines of capsules HT-14 and -15.

Table 4.1. Survival rates^a by visual inspection for Biso-coated ThO₂ particles in capsules HT-12 through HT-15

Holder no.	Sample	HT-12	HT-13	HT-14	HT-15
Low-temperature holders					
2	GGA 4252-08	100	0	2	^b
4	ORNL OR-1850	100	100	96	94
5	ORNL OR-1846	100	100	98	100
7	GGA 4252-00	100	92	2	13
8	ORNL OR-1840	100	100	100	100
10	GGA 4252-06	98	100	100	100
11	ORNL OR-1749	100	87	96	87
13	ORNL OR-1849	100	100	100	100
40	GGA 4252-02	100	100	100	55
42	ORNL OR-1838	100	100	100	100
43	GGA 4252-03	100	0	0	0
45	ORNL OR-1826	100	100	81	79
46	GGA 4252-01	100	68	0	0
48	ORNL OR-1830	100	100	100	96
49	GGA 4252-07	100	62	0	0
51	ORNL OR-1837	100	100	100	91
High-temperature holders					
15	GGA 4252-08	40	0	0	0
17	ORNL OR-1850	100	3	0	0
18	ORNL OR-1846	100	0	0	0
20	GGA 4252-00	97	0	0	0
21	ORNL OR-1840	100	100	100	7
23	GGA 4252-06	100	0	15	19
24	ORNL OR-1749	100	100	7	100
26	ORNL OR-1849	100	100	100	97
27	GGA 4252-02	100	12	11	0
29	ORNL OR-1838	100	100	97	100
30	GGA 4252-03	0	0	0	0
32	ORNL OR-1826	100	23	11	44
33	GGA 4252-01	73	0	0	0
35	ORNL OR-1830	100	0	0	0
36	GGA 4252-07	75	0	0	0
38	ORNL OR-1837	45	0	0	0

^aAll values reported as percent survived.

^bSample holder 2 was shipped to San Diego unopened

The Poco graphite sample holders located in the high-fluence, high-temperature magazines of capsules HT-13, -14, and -15 also experienced extreme swelling and degradation of the graphite. Based on the design dimensions, the diametrical changes ranged from <1% in the low-fluence, low-temperature holders to >7% for the high-fluence, high-temperature holders in HT-14, and >9% for holders in HT-15. Table 4.3 summarizes the dimensional changes for particle holders in capsules HT-14 and -15.

In addition to the swelling and degradation, the sample holders in the high-fluence, high-temperature regions of HT-15 were severely distorted. Many had an "hourglass" appearance, having expanded about 4% in the midsection and at least 8% at the ends. Figure 4.1 shows the appearance of an as-fabricated sample holder and the appearance after irradiation of sample holder No. 25 in magazine CP-61 and sample holder No. 36 in magazine CP-62.

Table 4.2. Dimensional changes for the high- and low-temperature graphite magazines for HT-14 and -15

Magazine No.	Outside diameter (in.)			Inside diameter (in.)	Length (in.)
	Large (0°/90°)	Midpoint (0°/90°)	Small (0°/90°)		
Preirradiation ^a					
CP-56,-59, -60,-63	0.5139/0.5129	<i>b</i>	0.5011/0.5001	0.388/0.386	4.311/4.309
CP-57,-58, -61,-62	0.4965/0.4955	<i>b</i>	0.4765/0.4755	0.388/0.386	4.311/4.309
Postirradiation					
CP-56	0.5165/0.5165	0.5134/0.5120	0.5060/0.5055	<i>b</i>	<i>b</i>
CP-57	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
CP-58	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
CP-59	0.5175/0.5173	0.5130/0.5140	0.5060/0.5055	<i>b</i>	<i>b</i>
CP-60	0.5186/0.5200	0.5130/0.5135	0.5088/0.5100	<i>b</i>	<i>b</i>
CP-61	0.5330/0.5323	0.5230/0.5234	0.5024/0.5065	<i>b</i>	<i>b</i>
CP-62	0.5222/0.5270	0.5215/0.5253	0.5022/0.5010	<i>b</i>	<i>b</i>
CP-63	0.5160/0.5162	0.5086/0.5077	0.5073/0.5068	<i>b</i>	<i>b</i>

^aPreirradiation dimensions are the same as design.^bDimensions were not measured.

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Fig. 4.1. Coated particle holders for loose particles irradiated in high-temperature (1500–1600°C) magazines in HT-15.

Table 4.3. Dimensional changes for particle holders in HT-14 and HT-15

Holder No.	Type of particle	HT-14				HT-15			
		Length (in.)	Percent change	Diameter (in.)	Percent change	Length (in.)	Percent change	Diameter (in.)	Percent change
Preirradiation									
		0.275/0.274		0.3855/0.3845		0.275/0.274		0.3855/0.3845	
Postirradiation									
1	U	0.2775	1.09	0.3900	1.30	0.2748	0.11	0.3885	0.91
2	ThO ₂					0.2732	-0.47	0.3887	0.96
3	U	0.2775	1.09	0.3884	0.88	0.2759	0.51	0.3888	0.99
4	ThO ₂					0.2788	1.57	0.3885	0.91
5	ThO ₂					0.2767	0.80	0.3876	0.68
6	U	0.2750	0.18	0.3880	0.78	0.2745	0.00	0.3868	0.47
7	ThO ₂					0.2750	0.18	0.3905	1.43
8	ThO ₂					0.2750	0.18	0.3893	1.12
9	U	0.2778	1.20	0.3885	0.91	0.2768	0.84	0.3889	1.01
10	ThO ₂					0.2775	1.09	0.3895	1.17
11	ThO ₂					0.2782	1.35	0.3910	1.56
12	U	0.2790	1.64	0.3890	1.04	0.2842	3.53	0.3910	1.56
13	ThO ₂					0.2761	0.58	0.3899	1.27
14	U					0.2937	6.99	0.4110	6.75
15	ThO ₂	0.2882	4.99	0.4038	4.88	0.3015	9.84	0.4170	8.31
16	U					0.3042	10.82	0.4180	8.57
17	ThO ₂	0.310	12.93	0.414	7.53	0.3150	14.75	0.4230	9.87
18	ThO ₂			0.412	7.01	0.2951	7.50	0.4216	9.51
19	U					0.2910	6.01	0.4153	7.88
20	ThO ₂	0.2965	8.01	0.4100	6.49	0.2910	6.01	0.4183	8.65
21	ThO ₂	0.301	9.65	0.411	6.75	0.2990	8.93	0.4197	9.01
22	U					0.2865	4.37	0.4178	8.52
23	ThO ₂	0.2960	7.83	0.4112	6.81	0.2928	6.67	0.4190	8.83
24	ThO ₂	0.296	7.83	0.410	6.49	0.2958	7.76	0.4180	8.57
25	U					0.2985	8.74	0.4170	8.31
26	ThO ₂	0.298	8.56	0.412	7.01	0.2964	7.98	0.4187	8.75
27	ThO ₂	0.291	6.01	0.406	5.45	0.2990	8.93	0.4195	8.96
28	U					0.3015	9.84	0.4177	8.49
29	ThO ₂	0.292	6.38	0.409	6.23	0.2932	6.81	0.4178	8.52
30	ThO ₂	0.2895	5.46	0.4063	5.53	0.2947	7.36	0.4168	8.26
31	U					0.2975	8.38	0.4135	7.40
32	ThO ₂	0.288	4.92	0.407	5.71	0.2948	7.40	0.4185	8.70
33	ThO ₂	0.2860	4.19	0.4033	4.75	0.3028	10.31	0.4180	8.57
34	U					0.2992	9.00	0.4210	9.35
35	ThO ₂	0.2875	4.74	0.4018	4.36	0.2973	8.31	0.4230	9.87
36	ThO ₂	0.2955	7.65	0.4030	4.68	0.298	8.56	0.4225	9.74
37	U					0.3002	9.36	0.4180	8.57
38	ThO ₂	0.2930	6.74	0.3990	3.64	0.3055	11.29	0.4207	9.27
39	U					0.2938	7.03	0.4164	8.16
41	U	0.2775	1.09	0.3880	0.78				
44	U	0.2775	1.09	0.3880	0.78				
47	U	0.2770	0.91	0.3885	0.91				
50	U	0.2768	0.84	0.3880	0.78				
52	U	0.2785	1.46	0.3990	3.64				

References

1. J. H. Coobs et al., "Irradiation Stability of Carbon Coatings on HTGR Fuel Particles," p. 249 in *11th Biennial Conference on Carbon, June 4-8, 1973*, CONF-730601, Sponsored by the American Carbon Committee and Oak Ridge National Laboratory.
2. J. H. Coobs, W. P. Eatherly, and J. L. Scott, "Testing and Irradiation Performance of Coated Particle Fuels for HTGR's," pp. 38.1-38.4 in *International Conference on Nuclear Fuel Performance, October 1973*, BNES 1974, Sponsored by the British Nuclear Energy Society.
3. General Atomic Company, *HTGR Fuels and Core Development Program Q. Prog. Rep. Aug. 30, 1974*, pp. 63-74, GA-A13126.

5. TEMPERATURE ANALYSIS

There are no provisions for direct temperature monitoring or for a sweep gas system in the HT capsules. Therefore, thermal modeling is used to predict maximum fuel operating temperatures. The design temperatures of 1250 and 900°C for the high- and low-temperature sleeves, respectively, are relevant because approximately 40% of the fuel in an HTGR core will operate at or above 900°C, and approximately 4% will operate at or above 1250°C.

The thermal modeling code HTCAP¹ was used to determine maximum operating temperatures for the fertile fuel particles in capsules HT-12 through HT-15. Maximum particle surface temperatures were calculated at two-day intervals for each HFIR irradiation cycle. Temperature calculations were based on knowledge of the dimensional change characteristics of the graphite sample holders, graphite magazines, and aluminum containment vessel as a function of temperature and fast neutron fluence ($E > 0.18$ MeV); fission heat generated per particle based on isotopic density changes as a function of time; gamma heating rates; changes in material thermal conductivities² as a function of temperature and fast neutron fluence ($E > 0.18$ MeV); and coolant temperatures at the containment surface. A detailed description of the calculational procedure is described in ref. 1.

Tables 5.1 through 5.3 describe in general the maximum particle surface temperature ranges of specific ORNL coated particle batches for each irradiation cycle. Coated particles in holders 2 through 13 and 42 through 51 were irradiated in the low-flux, low-temperature regions of each capsule. Holders 15 through 38 were irradiated in the high-flux, high-temperature regions of each capsule. Detailed time-temperature histories for each ORNL and GAC coated particle batch are described in Appendix A. For each particle holder in HT-12 through HT-15, the maximum particle surface temperature, the temperature at the outside diameter of the fueled annulus of the sample holder, and the power generated per ThO₂ particle are plotted as a function of time from the beginning of irradiation.

Table 5.1. Maximum particle surface temperatures for HT-12

Holder No.	ORNL particle batch	Particle diameter (μm)	Temperature range (°C) for HFIR cycles	
			82	83
4	OR-1850	694	980–1088	1175–1198
5	OR-1846	482	1005–1114	1209–1225
8	OR-1840	552	1013–1100	1195–1206
11	OR-1749	540	1025–1147	1257–1260
13	OR-1849	816	1152–1179	1293–1274
17	OR-1850	694	1305–1408	1526–1509
18	OR-1846	482	1315–1415	1543–1520
21	OR-1840	552	1314–1379	1495–1466
24	OR-1749	540	1319–1411	1532–1512
26	OR-1849	816	1477–1437	1566–1515
29	OR-1838	594	1319–1385	1501–1473
32	OR-1826	506	1314–1417	1540–1517
35	OR-1830	480	1315–1423	1546–1528
38	OR-1837	452	1497–1454	1578–1534
42	OR-1838	594	1025–1119	1224–1222
45	OR-1826	506	1013–1137	1238–1249
48	OR-1830	480	1065–1139	1237–1247
51	OR-1837	452	1104–1121	1209–1211

Table 5.2. Maximum particle surface temperatures for HT-13

Holder No	ORNL particle batch	Particle diameter (μm)	Temperature range ($^{\circ}\text{C}$) for HFIR cycles				
			83	84	85	86	87 ^a
4	OR-1840	694	980–1022	1048–1208	1228–1273	1295–1313	1333
5	OR-1846	482	1005–1046	1070–1239	1258–1302	1326–1342	1363
8	OR-1840	552	1013–1035	1061–1214	1236–1274	1294–1306	1328
11	OR-1749	540	1025–1073	1108–1274	1299–1335	1358–1370	1390
13	OR-1849	816	1152–1119	1152–1285	1316–1340	1369–1372	1395
17	OR-1840	694	1305–1328	1370–1528	1554–1576	1602–1606	1628
18	OR-1846	482	1315–1339	1378–1539	1563–1588	1615–1616	1642
21	OR-1840	552	1314–1311	1342–1480	1509–1529	1555–1551	1577
24	OR-1749	540	1319–1334	1376–1531	1558–1576	1603–1604	1625
26	OR-1849	816	1477–1386	1423–1534	1564–1572	1603–1594	1619
29	OR-1838	594	1319–1316	1350–1494	1522–1540	1567–1560	1586
32	OR-1826	506	1314–1338	1380–1539	1565–1588	1615–1613	1635
35	OR-1830	480	1315–1347	1383–1547	1571–1597	1623–1624	1650
38	OR-1837	452	1497–1399	1438–1548	1577–1594	1622–1617	1642
42	OR-1838	594	1042–1055	1082–1233	1258–1292	1317–1321	1344
45	OR-1826	506	1013–1058	1093–1265	1287–1326	1351–1363	1383
48	OR-1830	480	1065–1074	1103–1260	1279–1323	1342–1362	1377
51	OR-1837	452	1104–1076	1098–1222	1244–1279	1304–1320	1337

^aCapsule HT-13 was irradiated for one day during HFIR fuel cycle 87

Table 5.3. Maximum particle surface temperature for HT-14 and HT-15

HT-14 – Cycles 85 through 90
HT-15 – Cycles 85 through 91

Holder No	ORNL particle batch	Particle diameter (μm)	Temperature range ($^{\circ}\text{C}$) for HFIR cycles						
			85	86	87	88	89	90	91
4	OR-1840	694	980–1088	1115–1227	1288–1294	1311–1321	1338–1329	1346–1334	1382–1334
5	OR-1846	482	1005–1114	1144–1257	1317–1323	1340–1347	1364–1362	1377–1367	1410–1359
8	OR-1840	552	1013–1100	1127–1232	1293–1290	1307–1309	1328–1319	1336–1324	1371–1313
11	OR-1749	540	1025–1147	1180–1295	1359–1346	1371–1370	1390–1378	1398–1380	1431–1372
13	OR-1849	816	1152–1179	1212–1306	1377–1351	1377–1372	1395–1377	1400–1376	1431–1362
17	OR-1840	694	1305–1408	1442–1542	1616–1587	1611–1606	1627–1606	1630–1600	1659–1588
18	OR-1846	482	1315–1415	1455–1553	1629–1597	1620–1616	1639–1621	1641–1615	1673–1597
21	OR-1840	552	1314–1379	1410–1499	1567–1537	1558–1551	1571–1553	1573–1547	1605–1532
24	OR-1749	540	1319–1411	1449–1543	1620–1584	1611–1604	1622–1603	1624–1594	1654–1580
26	OR-1849	816	1477–1437	1481–1542	1629–1578	1611–1591	1616–1593	1617–1583	1648–1566
29	OR-1838	594	1319–1385	1418–1507	1583–1548	1570–1559	1586–1559	1583–1553	1613–1539
32	OR-1826	506	1314–1417	1454–1550	1629–1597	1623–1613	1632–1613	1636–1607	1668–1592
35	OR-1830	480	1315–1423	1463–1561	1637–1608	1631–1624	1647–1624	1647–1618	1679–1606
38	OR-1837	452	1497–1454	1491–1561	1643–1599	1629–1614	1639–1616	1642–1609	1677–1595
42	OR-1838	594	1025–1119	1147–1249	1316–1305	1325–1324	1341–1332	1354–1337	1385–1323
45	OR-1826	506	1013–1137	1167–1281	1345–1342	1364–1363	1383–1376	1396–1376	1429–1373
48	OR-1830	480	1065–1139	1166–1278	1337–1336	1361–1362	1384–1375	1397–1380	1428–1377
51	OR-1837	452	1104–1121	1145–1239	1296–1297	1314–1320	1342–1335	1352–1342	1387–1339

5.1 Discussion

The thermal analysis of capsules HT-12 through HT-15 indicated that this experiment was more severe than originally designed. The particle sample holders operated between 50 and 200° C higher than design temperatures, 900 and 1250° C, depending upon the holder location in the graphite magazine. The specimen holder temperatures by themselves were not adequate in describing particle operating temperatures. Maximum particle surface temperatures were found to exceed specimen holder temperatures by as much as 100° C after one cycle and to peak at approximately 300° C higher during the fourth cycle in the high-temperature regions and in the sixth cycle in the low-temperature regions. The particle surface operating temperatures in the low-temperature regions were 1200 to 1300° C, and in the high-temperature regions were 1500 to 1600° C. These ranges would apply to approximately 5% of the total fuel in an HTGR core for the low-temperature regions and less than 1% for the high-temperature regions.³

References

1. M. J. Kania, *HTCAP—A FORTRAN IV Program for Calculating Coated Particle Operating Temperatures in HFIR Target Irradiation Experiments*, ORNL/TM-5332 (May 1976).
2. J. P. Moore, R. S. Graves, and D. L. McElroy, "Thermal and Electrical Conductivities and Seebeck Coefficients of Unirradiated and Irradiated Graphites from 300 to 1000° K," *Nucl. Technol.* **22**, 88–93 (April 1974).
3. Del Marva Power and Light Co., "Preliminary Safety Analysis Report."

6. DETERMINATION OF BURNUP FROM FISSION PRODUCT INVENTORIES

Burnups were determined by two methods. In method 1, fission rate curves for ^{233}U and ^{235}U were produced by independent calculations, and the burnups were calculated through the use of those curves; fission product yields and fission product inventories were determined by gamma-ray spectroscopy. In method 2 the fission products produced and the burnups were calculated as a function of neutron flux by a direct solution to the modified Bateman equations involved in the actinide-to-fission-product chain. Measured values of fission product inventories were then compared with those data to obtain the burnups. The details of these calculations as well as the gamma-ray spectroscopy techniques are given in this chapter. A comparison is made of these burnup values with those calculated for nominal design conditions for the HFIR target position.

6.1 Gamma-Ray Spectroscopy of Individual Particles

Selected batches of coated particles were transferred from the High-Radiation-Level Examination Laboratory hot cells to a comparatively clean laboratory where the particles were separated, loaded singly into clean plastic vials, and assigned individual identification numbers. Each particle was then analyzed by gamma-ray spectroscopy.

The analyses were performed on a low-priority schedule and took about a year to complete. During this time, detectors and analyzer equipment changed. The analyzer systems were calibrated primarily with an International Atomic Energy Agency (IAEA) ^{137}Cs gamma-ray standard. Efficiencies at energies other than that of the ^{137}Cs gamma ray were determined using the multiple gamma rays of ^{226}Ra for which intensities and energies are well known.¹ A National Bureau of Standards ^{137}Cs gamma-ray calibration standard obtained later agreed well with the IAEA ^{137}Cs gamma-ray standard.

Many of the coated particles were leached to determine coating failures as described in Sect. 8. Some drifts in analytical results were noted during analyses of the same coated particles before and after leaching which could not be ascribed to loss of fission products during leaching. These drifts over a period of approximately a year amount to about +11% for ^{106}Ru , about +5% for ^{125}Sb , 0 to 4% for ^{137}Cs , and about +5% for ^{144}Ce . Only the earlier analyses were available for ^{95}Zr in most of the samples because of its shorter half-life. During the first part of the year, the systems were checked frequently with ^{137}Cs and only occasionally with ^{226}Ra . After the drifts were noticed, both nuclides were used for more frequent checks, and a coated particle was also used as a standard.

The analyses of ^{137}Cs are considered to be more accurate because of the frequent calibrations with the ^{137}Cs standard. Also, the ^{137}Cs gamma-ray peak is one of the most prominent in samples that have decayed for a long period. The standard deviation in count rate was influenced by decay time, but generally for these samples, the nuclides in order of increasing error in the count rate were ^{137}Cs , ^{144}Ce , ^{106}Ru , ^{125}Sb , and ^{95}Zr .

Averages of analytical data for groups of coated particles are given in Appendix B, Table B.1. Disintegration rates were changed to atoms of fission product per initial atom of thorium. The standard deviation (percent) for these values in each group of particles is also given, followed by the average standard deviation [percent (% error)] for the count rates of the individual particles as determined by the equation

$$\sigma(\%) = \frac{\sqrt{G+B}}{G-B} \times 100, \quad (1)$$

where

G = gross count,

B = baseline count in the gamma-spectrum peak of interest.

6.2 Method 1—Burnup Determination

The burnup determinations were calculated by a rather involved procedure. The counting data for the isotopes ^{95}Zr , ^{106}Ru , ^{137}Cs , and ^{144}Ce were normally considered. The measured disintegration rates for each isotope were corrected for the intensity of a particular energy peak¹ and for the decay occurring after the end of the irradiation.

In-reactor decay was calculated by a trapezoidal-rule approximation. For example, consider the calculations for ^{95}Zr . In the i th time increment,* t_i , the number of atoms of ^{95}Zr , $A_{\text{Zr},i}$, generated is

$$A_{\text{Zr},i} = (Y_{\text{Zr},3}\bar{F}'_{3,i} + Y_{\text{Zr},5}\bar{F}'_{5,i})t_i, \quad (2)$$

where

$Y_{\text{Zr},3}$ = yield of ^{95}Zr from ^{233}U fission in a thermal neutron flux, atoms per fission;

$Y_{\text{Zr},5}$ = yield of ^{95}Zr from ^{235}U fission in a thermal neutron flux, atoms per fission;

$\bar{F}'_{3,i}$ = average fission rate for ^{233}U during time increment t_i , fissions per unit time;

$\bar{F}'_{5,i}$ = average fission rate for ^{235}U during time increment t_i , fissions per unit time.

The fraction of ^{95}Zr left at the end of the irradiation, f_{Zr} , is thus

$$f_{\text{Zr}} = \frac{\sum_i A_{\text{Zr},i} \exp(-0.693t_i/\text{half-life})}{\sum_i A_{\text{Zr},i}}, \quad (3)$$

in which t_i is the decay time from the middle of the i th time increment to the end of the irradiation. The nominal time-dependent fission rates at the horizontal midplane (HMP) of the HFIR are calculated with the CACA-II² computer code, using cross sections in Table 6.1. Similar information was also available at other positions along the axis of the capsule. These data, together with the thermal neutron yields from Meek and Rider,³ were then used to calculate the fraction of either ^{95}Zr , ^{106}Ru , ^{137}Cs , or ^{144}Ce remaining at the end of each irradiation. (In the absence of information about yields for ^{234}Pa fission shown in Fig. 6.1, we assumed that ^{234}Pa fission could be apportioned equally between ^{233}U and ^{235}U fissions.) These fractional amounts are given in Table 6.1, together with the fraction of ^{233}U fissions for each irradiation. It should be noted that the fractional amounts of each isotope are primarily dependent on the total irradiation time and are not very sensitive to the fraction of ^{233}U fissions, as can be seen, for example, by comparing all the HT-13 values.

The burnup was calculated from the gamma spectroscopy data, the initial moles of actinide, and the fractional amounts given in Table 6.2. For example, the gamma spectroscopy disintegration rate for ^{95}Zr was divided by the fractional amount to give the fission-produced moles, M_{Zr} , by means of the relation

$$M_{\text{Zr}} = \frac{(\text{corrected disintegrations/sec})(\text{half-life, sec})}{(0.693)(\text{Avogadro's number})}. \quad (4)$$

*One 23-day HFIR cycle is an adequately small increment.

Table 6.1. Neutron cross sections used in calculations of fission products and burnup in HT-12 through HT-15 capsules

Nuclide	σ_f (barns)	σ_c (barns)	σ_a (barns)
Th-232	0.012	4.320	4.332
Pa-233		36.600	36.600
Pa-234	2000.000	200.000	2200.000
U-233	215.000	22.000	237.000
U-234		48.100	48.100
U-235	215.000	39.300	254.300
U-236		10.000	10.000
U-237		140.000	140.000
U-238	0.047	5.420	5.467
Np-237		60.000	60.000
Np-238	700.000	18.000	718.000
Np-239		11.000	11.000
Pu-238		160.000	160.000
Pu-239	351.000	153.000	504.000
Pu-240		356.000	356.000
Pu-241	442.000	142.000	584.000
Pu-242		35.000	35.000
Sr-90		0.800	0.800
Zr-95		0.000	0.000
Ru-106		0.146	0.146
Sb-125		0.000	0.000
Cs-137		0.110	0.110
Ce-144		1.000	1.000

Note: σ_f = fission cross section,
 σ_c = capture cross section,
 σ_a = total cross section.

Table 6.2. In-reactor decay factors and ^{233}U fission

Irradiation No.	Irradiation time (days)	Fraction remaining at discharge				Fraction ^{233}U fissions ^a
		^{95}Zr	^{106}Ru	^{137}Cs	^{144}Ce	
HT-12-26, -21	38.6	0.862	0.973	0.999	0.966	0.813
HT-13-26, -29	85.6	0.684	0.933	0.998	0.913	0.767
HT-14-26, -29	137.0	0.580	0.900	0.996	0.872	0.720
HT-15-26, -29	160.0	0.524	0.881	0.996	0.848	0.707
HT-13-21, -13	85.6	0.715	0.939	0.998	0.922	0.773
HT-14-21	137.0	0.583	0.901	0.996	0.873	0.727
HT-12-13	38.6	0.862	0.973	0.999	0.965	0.817
HT-14-13	137.0	0.595	0.904	0.997	0.878	0.749
HT-15-13	160.0	0.544	0.887	0.996	0.856	0.738
HT-12-8	38.6	0.860	0.973	0.999	0.965	0.820
HT-13-8	85.6	0.730	0.943	0.998	0.926	0.796
HT-14-8	137.0	0.601	0.907	0.997	0.881	0.758
HT-15-8	160.0	0.551	0.889	0.996	0.859	0.750
HRB6-1C-1, -2	184.0	0.279	0.763	0.991	0.717	0.331
P13LC4T6	423.5	0.297	0.754	0.990	0.698	1.00

^aFraction ^{235}U fission is $(1 - ^{233}\text{U} \text{ fraction})$. Protactinium-234 fissions were distributed evenly between ^{233}U and ^{235}U fissions.

Fig. 6.1. Nominal calculated fission rates and burnup in the target region of the HFIR at the horizontal midplane.

Finally, the burnup was calculated by the relation

$$\% \text{ FIMA} = \frac{100\% \times M_{Zr}}{(\text{initial moles actinide})(f_3 Y_{Zr,3} + f_5 Y_{Zr,5})}, \quad (5)$$

where

FIMA = fissions per initial heavy-metal atom,

f_3 = fraction ^{233}U fissions (Table 6.2),

f_5 = fraction ^{235}U fissions ($= 1 - f_3$).

6.3 Method 2—Determination of Burnup, Effective Neutron Flux, and Fission Product Inventories

Fission product inventories per original atom of thorium were calculated as a function of neutron flux, using the effective neutron cross sections for actinides in the A-2 type facilities of the HFIR. The cross sections used for the fission products are for thermal neutrons and were obtained from the tabulation by Goldberg et al.^{4,5,6} All of the cross sections used are presented in Table 6.1; the irradiation history is given in Table 3.1; geometry factors for distance from the horizontal midplane are given in Table 6.3. These are compared with geometry factors calculated from the ¹⁴⁴Ce analyses. The fission product yields are taken from a compilation by Meek and Rider,⁷ and half-lives are from the *GE Chart of the Nuclides*.⁸

Although many computer programs exist for determining fission product inventories and burnup,^{2,9,10} most of these involve extensive input and output data, many of which are not essential in certain problems. FORTRAN IV was used because it is easily adapted to change on the PDP-10; it fits various problems and produces the output in a convenient form. A shorthand notation for the generation of the modified Bateman equations¹¹ was developed which is easily adaptable to any nuclide production-decay chain and is easily translated to FORTRAN IV language.

The equations used for calculating the fission product inventories and burnup were derived by solving the differential equations for production, activation, and decay of the various nuclides in the chain from ²³²Th to fission products. The generalized solution is given as follows:

N_i = i th nuclide in chain (atoms at time t);

N_i^0 = original amount of i th nuclide in chain (atoms) at time 0;

$\alpha_i = (\Phi\sigma_a + \lambda)_i$ = loss rate term for the i th nuclide, where Φ = neutron flux (neutrons $\text{cm}^{-2} \text{sec}^{-1}$), σ_a = adsorption cross section (cm^2), and λ = decay constant (sec^{-1});

A_i = either of $\Phi\sigma_f$, $\Phi\sigma_c$, or λ as applicable for the production of the $(i+1)$ th nuclide from the i th nuclide, where σ_f = fission cross section (cm^2), and σ_c = activation cross section (cm^2);

$A_{i,m} = (\Phi\sigma_f\gamma)_i$ for production of fission product m from the i th nuclide, where γ = yield;

$C(i,j) = (\alpha_j - \alpha_i)^{-1}$;

$E(i) = \exp(-\alpha_i t)$, where t = irradiation time (sec);

$E(i,j) = C(i,j)[E(i) - E(j)]$;

$E(1,2,3, \dots, n) = C(1,2)[E(1,3,4, \dots, n) - E(2,3,4, \dots, n)]$.

Table 6.3. Geometry factors for neutron flux for the HT capsules

Note: 3.267 E+15 is read 3.267×10^{15}

Holder	Distance from HMP (in.)	Calculated factor	Neutron flux based on ¹³⁷ Cs (neutrons $\text{cm}^{-2} \text{sec}^{-1}$)	Geometry factor based on ¹⁴⁴ Ce analyses
8	7.21	0.66	3.267 E+15	0.66
13	5.80	0.77	3.812 E+15	0.75
21	2.21	0.94	4.653 E+15	0.95
29	1.37	0.97	4.802 E+15	1.00
26	0.80	0.99	4.900 E+15	0.96
HMP	0.00	1.00	4.950 E+15	1.00

Then

$$N_n = \left[\prod_{i=1}^{n-1} A_i \right] N_1^0 E(1, 2, \dots, n) + \left[\prod_{i=2}^{n-1} A_i \right] N_2^0 E(2, 3, \dots, n) + \dots + A_{n-1} N_{n-1}^0 E(n-1, n) + N_n^0 E(n). \quad (6)$$

The nuclide production chain is shown in Fig. 6.2. Parallel sections in the chain are solved by special adaptations.

The burnup (fissions per original atom of thorium or FIMA) was calculated by

$$\text{FIMA} = 1 - \sum_{i=1}^J N_i, \quad (7)$$

where N_i = concentration of the i th actinide and J = total number of actinides in ^{232}Th chain of Fig. 6.2.

The calculated fission product inventories are given in Appendix B, Tables B.2 through B.5. The analyzed concentrations of several fission products were used to obtain neutron fluxes by interpolation of the calculated values in Tables B.6 through B.9. These neutron fluxes are given in Table 6.4. The average values derived from ^{95}Zr , ^{106}Ru , and ^{144}Ce are also presented in the table. Values from ^{125}Sb and ^{137}Cs were omitted from the averages because these fission products were lost at high temperatures during irradiation. The average neutron flux for each holder was divided by the calculated geometry factor for distance from the horizontal midplane in the reactor in order to calculate the maximum neutron flux from each coated-particle sample. The average of these values, weighted according to the

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Fig. 6.2. Chain for the production of fission products from ^{232}Th .

Table 6.4. Effective neutron fluxes for HT-12 through HT-15 irradiation experiments calculated from fission product inventories in BISO-coated ThO₂ particles

Note: 2.704 E+15 is read 2.704 × 10¹⁵

Experiment	Number of particles examined	Attenuation factor	Neutron flux (neutrons cm ⁻² sec ⁻¹) from inventories of:					Average ^a neutron flux (neutrons cm ⁻¹ sec ⁻¹)	Average ^b neutron flux at HMP (neutrons cm ⁻² sec ⁻¹)
			⁹⁵ Zr	¹⁰⁶ Ru	¹⁴⁴ Ce	¹²⁵ Sb	¹³⁷ Cs		
HT-12-8	16 ^c	0.66	2.704 E+15	3.268 E+15	3.024 E+15	3.459 E+15	3.278 E+15	2.999 E+15	4.544 E+15
HT-12-13	16 ^c	0.77	3.136 E+15	3.656 E+15	3.442 E+15	3.917 E+15	3.726 E+15	3.411 E+15	4.430 E+15
HT-12-21	16 ^c	0.94	3.664 E+15	4.530 E+15	4.277 E+15	4.803 E+15	4.644 E+15	4.157 E+15	4.422 E+15
HT-12-26	15 ^c	0.99	3.948 E+15	4.543 E+15	4.356 E+15	4.926 E+15	4.729 E+15	4.282 E+15	4.325 E+15
HT-12-26	1 ^d	0.99	3.594 E+15	3.985 E+15	4.146 E+15	4.926 E+15	4.644 E+15	3.908 E+15	3.947 E+15
HT-13-8	15 ^c	0.66	2.611 E+15	3.321 E+15	3.064 E+15	3.397 E+15	3.386 E+15	2.999 E+15	4.544 E+15
HT-13-8	1 ^d	0.66	2.729 E+15	3.123 E+15	2.997 E+15	3.280 E+15	3.306 E+15	2.950 E+15	4.470 E+15
HR-13-13	15 ^c	0.77	3.000 E+15	3.827 E+15	3.521 E+15	3.744 E+15	3.906 E+15	3.449 E+15	4.479 E+15
HT-13-21	18 ^c	0.94	4.055 E+15	4.488 E+15	4.309 E+15	4.053 E+15	3.923 E+15	4.284 E+15	4.557 E+15
HT-13-26	19 ^c	0.99	3.961 E+15	4.700 E+15	4.410 E+15	4.582 E+15	3.957 E+15	4.357 E+15	4.401 E+15
HT-13-29	18 ^e	0.97	4.209 E+15	4.909 E+15	4.561 E+15	4.698 E+15	4.786 E+15	4.560 E+15	4.701 E+15
HT-14-8	1 ^c	0.66	2.661 E+15	3.230 E+15	2.905 E+15	3.120 E+15	3.443 E+15	2.932 E+15	4.442 E+15
HT-14-8	15 ^d	0.66	2.734 E+15	3.288 E+15	3.005 E+15	3.000 E+15	3.327 E+15	3.009 E+15	4.559 E+15
HT-14-13	17 ^f	0.77	3.322 E+15	3.870 E+15	3.488 E+15	3.382 E+15	3.539 E+15	3.560 E+15	4.623 E+15
HT-14-21	12 ^c	0.94	4.377 E+15	3.230 E+15	4.697 E+15	4.194 E+15	3.139 E+15	4.101 E+15	4.363 E+15
HT-14-21	3 ^d	0.94	4.354 E+15	5.068 E+15	4.497 E+15	3.647 E+15	<2.4 E+15	4.640 E+15	4.936 E+15
HT-14-26	1 ^e	0.99	4.829 E+15	5.057 E+15	4.838 E+15	4.017 E+15	2.413 E+15	4.908 E+15	4.958 E+15
HT-15-8	13 ^b	0.66	2.909 E+15	3.341 E+15	2.985 E+15	2.994 E+15	<2.4 E+15	3.078 E+15	4.664 E+15
HT-15-13	1 ^c	0.77	3.352 E+15	3.995 E+15	3.490 E+15	3.390 E+15	3.418 E+15	3.612 E+15	4.691 E+15
HT-15-13	7 ^d	0.77	3.276 E+15	4.143 E+15	3.432 E+15	3.237 E+15	<2.4 E+15	3.617 E+15	4.697 E+15
HT-15-26	19 ^c	0.99	4.262 E+15	4.866 E+15	4.470 E+15	3.175 E+15	3.619 E+15	4.533 E+15	4.579 E+15
HT-15-29	19 ^e	0.97	4.525 E+15	5.323 E+15	4.657 E+15	3.756 E+15	2.541 E+15	4.835 E+15	4.985 E+15
Weighted average									4.5608 E+15

^aAverage does not include data from ¹²⁵Sb and ¹³⁷Cs.

^bAverage at HMP obtained by dividing the average neutron flux for each holder by its attenuation factor for distance from the HMP.

^cParticle coating survival as determined by hot chlorine leaching.

^dParticle coating failure as determined by hot chlorine leaching.

^eCoated particles not tested by hot chlorine leaching.

^fCoated particles used included both intact and failed coatings.

number of coated particles in the samples analyzed, was 4.6×10^{15} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. The coated-particle samples used in these calculations were separated into groups with intact, failed, or untested coatings. Coating failure caused no apparent release of ^{95}Zr , ^{106}Ru , or ^{144}Ce , as will be discussed in Sect. 9.1, and this is also indicated in the similar values of neutron fluxes calculated from these fission product inventories in intact and failed coated particles from the same batch and irradiation holder.

The burnups were determined by the same procedure as were the neutron fluxes, using the fission product inventories and the tables in Appendix B.

6.4 Results and Discussion

The average burnup values as computed by methods 1 and 2 for all coated particles in a given set are given in Table 6.5. The values obtained from ^{95}Zr , ^{106}Ru , and ^{144}Ce analyses were averaged in the last column. Values from ^{137}Cs were omitted from the final averages because these fission products are partially lost during irradiation to high burnups and temperatures. The same data from the B samples, Table 6.5, were used in calculations by both methods. The results indicate that the methods are equivalent.

It should be noted that burnups calculated from ^{95}Zr and ^{144}Ce are nearly equal, whereas those from ^{106}Ru are higher. In coated particles irradiated to lower burnups at the lower temperatures where cesium was apparently not lost, values calculated from ^{137}Cs inventories were higher than those of the other three isotopes. The lower burnups calculated from ^{137}Cs at higher temperatures and burnups reflect the cesium loss in these samples. The wide variations are possibly due to errors in geometry factors and cross sections or to the difference between the actual yields in the HFIR and the thermal neutron yields from Meek and Rider. An additional inconsistency is seen in a comparison of the burnups determined from the fission product inventories with those calculated by other methods, using data from conventional dosimetry. This comparison is illustrated by the plot of burnups in Fig. 6.3. The bars on the data points represent the range of the burnups determined from ^{95}Zr , ^{106}Ru , and ^{144}Ce inventories. The calculated burnups are given in the summary of burnups and neutron fluxes in Table 6.6.

A linear least-squares fit for a line forced through the origin was calculated for the data for each irradiation holder. The slope (b) is proportional to the variation between the burnups determined from fission product inventories and those calculated conventionally. The slope and the distance of the holder from the HMP of the reactor are given in the table inset in Fig. 6.3 and are plotted in Fig. 6.3b. The increase in b with the distance may indicate an error in the geometry factors used in the calculations of the burnup.

Table 6.5. Burnup values for HT-12 through HT-15 Biso-coated ThO₂ particles from fission product inventories

Sample No ^a	Burnup calculation method	Number of particles	Burnup in % FIMA from inventory of				Average ^b
			⁹⁵ Zr	¹⁰⁶ Ru	¹⁴⁴ Ce	¹³⁷ Cs	
HT 12-8-B	1	16	0 73	0 90	0 84	1 00	0 82
-B	2	16	0 71	0 95	0 84	0 96	0 83
HT-13-8-A	1	6	3 54	3 47	3 41	4 09	3 47
B	1	15	3 13	4 14	3 87	4 61	3 71
-B	2	15	3 15	4 33	3 90	4 44	3 79
HT-14-8-A	1	6	7 67	7 67	7 28	8 56	7 54
-B	1	15	7 23	8 62	7 96	9 41	7 94
-B	2	15	7 21	8 97	8 07	9 09	8 08
HT-15-8-A	1	6	9 31	9 18	9 70	6 57	9 06
-B	1	13	9 65	11 0	9 88	7 25	10 2
-B	2	13	9 77	11 4	10 1		10 4
HT-12-13-B	1	16	0 91	1 08	1 04	1 22	1 01
-B	2	16	0 89	1 14	1 03	1 17	1 02
HT-13-13-B	1	15	3 82	5 01	4 66	5 55	4 50
-B	2	15	3 79	5 20	4 67	5 34	4 55
HT-14-13-A	1	6	9 71	9 38	8 85	10 2	9 31
-B	1	17	9 14	10 6	9 50	10 1	9 75
-B	2	17	9 08	10 8	9 61	9 77	9 83
HT-15-13-A	1	6	11 7	10 9	10 6	7 28	11 1
-B	1	7	11 3	13 5	11 6	6 92	12 1
-B	2	7	11 2	13 8	11 8		12 3
HT-12-21-B	1	16	1 16	1 52	1 45	1 71	1 38
-B	2	16	1 14	1 58	1 45	1 64	1 39
HT-13-21-A	1	10	6 01	6 18	6 08	5 82	6 09
-B	1	18	5 63	6 23	6 02	5 56	5 96
-B	2	18	5 60	6 37	6 05	5 37	6 01
HT-14-21-A	1	8	13 5	14 1	12 9	8 44	13 5
-B	1	12	12 7	15 3	13 4	9 09	13 8
-B	2	12	12 5	15 3	13 5	8 49	13 8
HT-12-26-A	1	5	1 55	1 42	1 43	1 89	1 47
-B	1	15	1 28	1 53	1 49	1 75	1 43
-B	2	15	1 28	1 58	1 49	1 68	1 45
HT-13-26-A	1	7	7 16	6 58	6 30	5 44	6 68
-B	1	19	5 68	6 66	6 37	5 85	6 24
-B	2	19	5 44	6 76	6 23	5 43	6 14
HT-14-26-A	1	5	15 5	15 5	14 0	9 65	15 0
-B	1	1	14 1	14 9	13 9	6 48	14 3
-B	2	1	14 0	14 7	14 0	6 20	14 3
HT-15-26-A	1	10	17 7	17 7	16 3	14 0	17 2
-B	1	19	15 2	17 1	15 6	12 9	16 0
-B	2	19	15 0	17 3	15 8	12 5	16 0
HT-13-29-A	1	6		6 71	6 46	7 10	
-B	2	18	5 87	7 14	6 50	9 62	6 50
HT-14-29-A	1	6	13 7	19 7	13 4	5 14	14 3
HT-15-29-A	1	6	15 8	17 7	15 6	5 55	16 4
-B	1	19	16 1	18 9	16 3	8 72	17 1
-B	2	19	16 0	19 1	16 5	8 36	17 2

^aConsists of the irradiation holder number followed by a letter indicating a particular group of particles from that holder. The data from the B groups were used in calculations by both methods as a comparison

^bDoes not include the burnup calculated from ¹³⁷Cs

Fig. 6.3. Comparison of calculated burnups vs burnups determined from fission products.

Table 6.6. Irradiation summary for capsules HT-12 through HT-15

Sample holder Nos		Distance from specimen holder to HMP (in)	Thermal flux ^a	Fast flux ^b	Fast flux ^c	Ratio, fast/thermal		Fertile particle burnup (% FIMA)			
						b/a	c/a	HT-12	HT-13	HT-14	HT-15
Low temperature											
2	51	8 909	1 75	1 41	0 59	0 81	0 42	0 95	4 53	9 56	11 91
4	49	8 344	1 87	1 57	0 67	0 84	0 43	1 06	5 00	10 45	13 00
5	48	8 061	1 93	1 67	0 70	0 87	0 42	1 10	5 20	10 90	13 50
7	46	7 496	2 05	1 85	0 76	0 90	0 41	1 21	5 62	11 67	14 42
8	45	7 214	2 11	1 92	0 80	0 91	0 42	1 26	5 84	12 05	14 90
10	43	6 649	2 24	2 08	0 85	0 93	0 41	1 37	6 22	12 75	15 72
11	42	6 366	2 31	2 16	0 88	0 94	0 41	1 40	6 40	13 08	16 10
13	40	5 801	2 42	2 30	0 93	0 95	0 40	1 50	6 75	13 70	16 82
High temperature											
15	98	3 909	2 83	2 70	1 08	0 95	0 39	1 71	7 70	15 30	18 72
17	36	3 344	2 94	2 80	1 09	0 95	0 39	1 78	7 90	15 67	19 12
18	35	3 061	3 00	2 83	1 11	0 94	0 39	1 80	8 00	15 82	19 32
20	33	2 496	3 10	2 91	1 13	0 94	0 39	1 82	8 15	16 10	19 65
21	32	2 214	3 13	2 94	1 14	0 94	0 39	1 86	8 21	16 21	19 80
23	30	1 649	3 19	3 00	1 16	0 94	0 39	1 90	8 33	16 42	20 03
24	29	1 366	3 22	3 03	1 16	0 94	0 38	1 91	8 38	16 50	20 15
26	27	0 081	3 25	3 11	1 17	0 96	0 38	1 92	8 43	16 60	20 30

^aneutrons cm⁻² sec⁻¹, $E < 1.86 \text{ eV} \times 10^{-15}$ ^bneutrons cm⁻² sec⁻¹, $E > 1.86 \text{ eV} \times 10^{-15}$ ^cneutrons cm⁻² sec⁻¹, $E > 0.18 \text{ MeV} \times 10^{-15}$

References

1. Reactor Shielding Information Center, *Radioactive Decay Gamma-ray Spectra Compilation, Nuclear Data Tables*, DLC-19, ORNL.
2. E. J. Allen, *CACA-2: Revised Version of CACA—A Heavy Isotope and Fission-Product Concentration Calculational Code for Experimental Irradiation Capsules*, ORNL/TM-5266 (February 1976).
3. M. E. Meek and B. F. Rider, *Compilation of Fission Product Yields*, NEDO-12154, Vallecitos Nuclear Center (1972).
4. M. D. Goldberg, S. F. Mughabghab, B. A. Magurno, V. M. May, *Neutron Cross Sections*, vol. IIA, BNL-325, 2d ed., Suppl. 2 (1966).
5. M. D. Goldberg, S. F. Mughabghab, S. N. Purohit, B. A. Magurno, V. M. May, *Neutron Cross Sections*, vol. IIB, BNL-325, 2d ed., Suppl. 2 (1966).
6. J. R. Stehn, M. D. Goldberg, R. Wiener-Chasman, S. F. Mughabghab, B. A. Magurno, V. M. May, *Neutron Cross Sections*, vol. III, BNL-325, 2d ed., Suppl. 2 (1965).
7. M. E. Meek and B. F. Rider, *Compilation of Fission Product Yields*, NEDO-12154-1, Vallecitos Nuclear Center, General Electric Co. (1974).
8. N. E. Holden and F. W. Walker, *Chart of the Nuclides, 11th Edition*, Knolls Atomic Power Laboratory, General Electric Co. April 1972.
9. H. H. Van Tuyl, *ISOGEN—A Computer Code for Radioisotope Generation Calculations*, HW-83785 (1964).
10. M. J. Bell, *ORIGEN, The ORNL Isotope Generation and Depletion Code*, ORNL-4628 (1973).
11. H. Bateman, "The Solution of a System of Differential Equations Occurring in the Theory of Radioactive Transformations," *Proc. Cambridge Philos. Soc.* **15**, 423 (1910).

7. MEASUREMENT AND INTERPRETATION OF IN-PARTICLE CARBON MONOXIDE AND KRYPTON + XENON

Particles from the HT-12 through -15 experiments, as well as from ORNL HRB-6 and GAC P13LC4T6 experiments, were used to determine internal gas pressures. The gases are primarily carbon monoxide, krypton, and xenon and are released from the kernel into the particle void space during fission. A knowledge of the burnup dependence of the in-particle Kr + Xe pressures is useful both for the particle pressure-vessel design and for fission-gas availability terms for particles failing in-reactor. The CO pressures can be equivalent to those for Kr + Xe and thus also affect the pressure-vessel design. More significantly, they can be used to infer the oxidation state of the fuel and fission products during burnup. This section will describe the measurement techniques, present the data, and interpret the results obtained to date in this continuing program.

7.1 Experimental Procedures and Results

The apparatus used for the pressure measurements has been described.¹ In this apparatus a particle is equilibrated at 1000 to 2000° C and broken to release the gases into a known volume. The pressure is measured with a capacitance manometer, and then a titanium wire is heated to ~900° C to getter the CO as well as traces of CO₂, leaving the pressure of Kr + Xe to be measured subsequently.

A primary concern of this program has been the validity of the CO measurements. For some time it was not conclusively demonstrated whether the CO measurements resulted from the real CO content in the particle before it was broken or from CO produced by rapid oxide-carbon chemical reactions after it was broken. These problems were considered in part in ref. 1. This question has apparently been favorably resolved by measurements completed on Harwell 919/8 particles obtained from Horsley² (AERE-Harwell) and M. Wagner-Löffler (Dragon Project). These low-enriched Triso particles experienced 5.7% FIMA, with 50% of the burnup being plutonium fissions. Particles from this batch were used to compare results of the mass spectrographic technique used at AERE-Harwell³ and at OSGAE (Austria)⁴ with the ORNL technique.¹

The experimental results are given in Table 7.1. The ORNL results for Kr + Xe through 1700° C average 2.73 mm³ (STP) and agree with the OSGAE results. The somewhat lower AERE results for Kr + Xe may be caused by a difference in the particle breaking method; at AERE the coatings are cracked with a micrometer to release the gas, whereas at ORNL and probably at OSGAE both the coating and the kernel are fractured, thus possibly releasing more gas from closed voids. The ORNL Kr + Xe release at 2000° C is higher than the lower-temperature results probably because of Kr + Xe diffusion from the kernel during the 2000° C equilibration.

The CO + CO₂ data at 1000° C lie between the AERE and OSGAE results; there does not appear to be any effect of delay time before breaking the particle nor of equilibrating for 1 hr or for 24 hr. At 1400° C the ORNL results agree with the OSGAE data when the particles are broken after a delay time of either 10 or 120 sec. (At OSGAE a 10-sec delay time is used,² whereas a 120-sec delay is used at Harwell.³) On the other hand, breaking the particles immediately results in a higher amount of CO + CO₂ (essentially CO). The difference between the delay-vs-no-delay results increases even more at 1700 and 2000° C. It would appear that breaking the particle at the higher temperatures might release some additional CO as a result of post-breaking reactions; this subject is being investigated with additional HT particles. Generally, however, these data compare very well and appear to validate the measurements by the European mass spectrometric method and the ORNL capacitance manometer technique.

Table 7.1. Gas volumes (mm³ at STP) in 919/8 particles

Temperature (°C)	AERE		OSGAE		ORNL		Time ^a
	Kr + Xe	CO + CO ₂	Kr + Xe	CO	Kr + Xe	CO + CO ₂	
1000	1.89	0.76	~2.8 ^b	1.1	2.89 2.44	0.94 0.96	24/0 1/120 ^c
1200	2.43	0.92	~2.8 ^b	1.6			
1400	2.16	1.21	~2.8 ^b	2.1	3.05 2.84 2.70	2.88 2.13 2.26	24/0 24/10 1/155
1700					2.79 2.87 2.33	3.80 2.50 0.24 ^d	1/0 1/120 1/120
2000 ^e					2.70 4.07 3.34	1/120 9.56 3.46	1/120 1/0 ^e 1/120 ^e

^aTime at temperature in hours/delay in seconds after heater was turned off and before breaking particle.

^bAverage of all AERE data times 1.3 (see ref. 2).

^cStandard AERE treatment (see ref. 3).

^dThis corresponds to in-particle P_{CO} over the SiC-SiO₂-CO equilibrium.

^eHeated at 1400°C for 50 min and then at 2000°C for 10 min.

Most of the present data were collected before the ORNL-AERE-OSGAE intercomparison was performed. Particles were generally broken at temperature after equilibration for 20 to 24 hr between 1000 to 1400°C, for 2 to 6 hr at 1500 to 1700°C, and for 2 to 5 min at 2000°C after 2 to 3 hr at 1700°C. (The intercomparison experiments show that long times at lower temperatures appear unnecessary; an hour is sufficient.) The data from the individual experiments are given in Table 7.2.

7.2 Krypton + Xenon Release from the Kernel

The percent release of Kr + Xe to the particle void space is shown in Fig. 7.1. This was calculated from the observed moles of Kr + Xe per fission and the theoretical yield. The theoretical amount of Kr + Xe was taken to be 0.335 per ²³³U fission and 0.306 per ²³⁵U fission; the yield of ¹³⁵Xe with a half-life of 9.17 hr is normally included because its large cross section results in the generation of stable ¹³⁶Xe. (Correspondingly, ¹³⁵Cs is not formed, and the total yield of cesium is that for ¹³³Cs and ¹³⁷Cs, ~12.3% for either ²³³U or ²³⁵U fission in a thermal flux.) The interpretation of the Kr + Xe results with regard to particle failure determination will be presented in Sect. 8.2.

7.3 Oxygen Release per Fission

Oxygen release per fission was calculated from the experimental release of CO (Table 7.2) and the burnup (Table 6.5). Many of the particles in this study were considered to be failed particles, as generally evidenced by abnormally low Kr + Xe contents as well as little or no CO. Only the oxygen release data from intact particles were considered; the corresponding CO data points are underlined in Table 7.2. The oxygen release per fission is plotted in Fig. 7.2; all of these data were fitted to the equation

$$O/f = (a + bf) \exp(-Q/RT), \quad (7.1)$$

where O/f is the measured moles of atomic oxygen released (as CO + CO₂) per mole of actinide that fissioned, f is the fraction FIMA (not % FIMA), Q is the apparent activation energy, R is the gas

Table 7.2. Equilibration temperatures and moles of CO and Kr + Xe

Irradiation No.	Particle type ^a	Moles $\times 10^8$											
		Kr + Xe						CO					
		particle number						particle number					
		1	2	3	4	5	6	1	2	3	4	5	6
HT-12-26	1	ND ^b	0.17	0.25				ND (1400) ^c	0.062 (1410)	ND (2000)			
HT-13-26	1	3.0	2.9	4.2	3.4	3.0	3.3	<u>0.43</u> ^d (1400)	<u>0.96</u> (1695)	<u>0.60</u> (2000)	<u>0.48</u> (1050)	<u>3.4</u> (2000)	<u>2.1</u> (1375)
HT-14-26	1	8.3	9.1	9.7	8.7	11.0		<u>6.3</u> (1400)	<u>11.0</u> (1700)	<u>23.0</u> (2000)	<u>2.0</u> (1080)	<u>6.1</u> (1100)	
HT-15-26	1	13.	EX ^e	13.	14.		EX	<u>11.0</u> (1400)	EX (1100)	<u>0.81</u> (1100)	<u>11.0</u> (1700)		EX (1100)
HT-13-21	2	0.87	1.5	1.3	1.6	1.5	1.4	<u>0.11</u> (1100)	<u>0.18</u> (1115)	<u>0.29</u> (2000)	<u>1.7</u> (1700)	<u>0.82</u> (1700)	<u>0.45</u> (1400)
Second set	2	1.8	1.4	1.3	0.68			1.1 (1700)	1.4 (2000)	0.53 (1550)	ND (1850)		
HT-14-21	2		ND	4.2	0.40	ND			ND (1100)	1.0 (1700)	ND (1400)	ND (1700)	
Second set	2	EX	EX	4.4	4.2			EX (1700)	EX (1700)	ND (1100)	2.3 (1700)		
HT-14-13	1	EX	0.21	0.43	5.5	EX	4.1	EX (1400)	0.28 (1700)	ND (1100)	6.4 (1430)	EX (1100)	ND (1100)
HT-15-13	1	0.19		EX	1.1			0.27 (1700)		EX (1600)	0.39 (1700)		
HT-13-8	2	0.13	0.29	0.14	0.14	0.07	0.10	<u>0.15</u> (1100)	<u>0.35</u> (1750)	<u>0.14</u> (1390)	<u>0.35</u> (1550)	<u>0.17</u> (1250)	1.25 (1400)
HT-14-8	2				0.34	ND	0.31				0.45 (1650)	ND (1850)	0.31 (1400)
HT-15-29	3	0.45	0.60	4.0	0.13		0.20	0.062 (1400)	ND (1665)	0.47 (1400)	1.1 (2000)		0.088 (1100)
HT-13-29 ^f	3	1.02	1.32	1.18	0.96	1.16	1.09	1.50 (2000)	0.15 (1400)	0.81 (1700)	ND (1100)	0.02 (1080)	0.98 (1400)
HT-14-29 ^f	3	EX	EX	ND	ND	0.44	0.21	EX (1400)	EX (1250)	ND (1400)	ND (1090)	0.15 (1375)	ND (1660)
HRB6-C1-1	4	5.1	4.8	4.7	4.6	5.2	4.6	<u>9.3</u> (2000)	<u>3.2</u> (1700)	<u>3.6</u> (1430)	<u>6.6</u> (1550)	<u>1.7</u> (1225)	<u>2.0</u> (1090)
	(Triso)												
HRB6-1C-2	4	4.9	4.8	4.9	5.1	6.3	5.0	<u>6.7</u> (1700)	<u>3.7</u> (1400)	<u>1.3</u> (1100)	<u>8.1</u> (2000)	<u>4.6</u> (1400)	<u>1.6</u> (1100)
P13LC4T6-10	5	0.46	1.2	0.50	1.1			<u>0.70</u> (1700)	<u>0.078</u> (1215)	<u>0.35</u> (1550)	<u>1.5</u> (2000)		
P13LC4T6-11	5	0.61	1.6	0.47	0.31			<u>1.1</u> (1800)	<u>1.1</u> (1700)	<u>0.065</u> (1100)	<u>0.12</u> (1400)		

^aKernel radius/buffer thickness, in μm : 1, 254/79.4; 2, 201/24.6; 3, 201/32.3; 4, 175/100; 5, 260/69.^bND = none detected.^cNumbers in parentheses indicate temperature in degrees centigrade.^dUnderlined values were used for the least-squares fit of Eq. 1 of Sect. 7.^eEX = particle exploded during observation through optical pyrometer.^fData added at last stages of report preparation; data not analyzed in text.

Fig. 7.1. Percent of theoretical Kr + Xe released by breaking individual irradiation particles. The open or closed symbol is the average value, while the vertical bars represent the data range. This Kr + Xe is assumed to exist primarily in the void space of the buffer layer.

constant, and T is the temperature in $^{\circ}\text{K}$. The coefficients a , b , and Q were determined from an application of the least-squares theorem simultaneously to all the data to give $a = 0.234$, $b = 26.5$, and $Q = 10,900$ cal/mole. These coefficients are applicable over the range $0.03 \leq f \leq 0.22$ and $1050 \leq T \leq 2000^{\circ}\text{C}$.

In-particle pressures of $\text{CO} + \text{CO}_2$ were calculated from the observed CO release by assuming that the ideal-gas law was valid at all pressures and that the available void space was 50% of the buffer-layer volume and 3% of the kernel volume. The chemical potential of oxygen ($\Delta\bar{F}_{\text{O}_2}^0 = RT \ln P_{\text{O}_2}$ for the reaction type $\text{M} + \text{O}_2 \rightarrow \text{MO}_2$ —henceforth called oxygen potential) was also calculated by assuming equilibrium in the $\text{C-CO-CO}_2\text{-O}_2$ system within the particle. These calculated results are given in Fig. 7.3.

7.4 Review of Oxide Fuel Chemistry

Interpretation of the observed oxygen release will be based on the FIMA-dependent composition of the particles and on the thermodynamic information that appears in the literature. The relative

Fig. 7.2. Experimental atomic oxygen release per fission in ThO_2 and $\text{Th}_{0.81}\text{U}_{0.19}\text{O}_2$ particles as a function of ^{233}U plus ^{235}U burnup and equilibration temperature. The four lines are from the least-squares fit of Eq. (7.1).

concentrations of all metals that may form oxides under conditions that may exist in a ThO_2 particle appear in Fig. 7.4. The total burnup and concentrations of ^{232}Th , ^{233}Pa , and $^{233-236}\text{U}$ are calculated as a function of exposure time at the HFIR horizontal midplane.⁵ The concentrations of fission products two years after reactor discharge were calculated from the burnup and from the Meek and Rider⁶ fission product yields for ^{233}U fission. Minor variations between ^{233}U and ^{235}U fission product yields are not significant to the analysis to be given here.

The majority of the available thermodynamic information on the chemical potential of oxygen for the actinide-fission product oxide systems is given in Fig. 7.5. The protactinium oxidizes in the range PaO_2 to $\text{PaO}_{2.5}$, and the information in Fig. 7.5 is from Knoch and Schieferdecker.⁷ The protactinium concentrations of interest here also exist in ThO_2 solid solutions at oxidation states ranging from PaO_2 to $\text{PaO}_{2.5}$.⁸ The UO_{2+x} system also exists in solid solution with ThO_2 ; hyperstoichiometry in the ThO_2 - UO_{2+x} system appears to occur at the same oxygen potential as in the pure UO_{2+x} system,⁹⁻¹¹ but values of $x \geq 0.001$ in the UO_{2+x} system do not occur at oxygen potentials more negative than -70 kcal/mole. Thus, the Th-U-Pa-O system appears to be a complete solid solution at the concentrations and oxygen potentials of interest here, with the protactinium at this point of the analysis being the only actinide above a 4+ valence state.

Fig. 7.3. Experimentally derived chemical potential of oxygen ($\Delta\bar{F}_{\text{O}_2}^0$) vs temperature and ^{233}U plus ^{235}U burnup in ThO_2 and $\text{Th}_{0.81}\text{U}_{0.19}\text{O}_2$ particles. Also indicated is the in-particle value of $P_{\text{CO}} + P_{\text{CO}_2}$ in atmospheres

Fig. 7.4. Time-dependent concentrations of actinides and fission products in the HFIR target region at the fission rate conditions shown in Fig. 6.1. Fission product yields are for ^{233}U fission in a thermal flux and also approximate those for ^{235}U fission. Cerium is shown separately from the other rare-earth elements for thermodynamic reasons. Also shown are total out-of-reactor U concentration after complete 27-day ^{233}Pa decay and the Pa and U concentrations in an HTGR.

Fig. 7.5. Literature values of $\Delta \bar{F}_{O_2}^0$ for several actinide, fission product, and Na systems. The Cs-Rb-U-O systems are believed to behave nearly identically to the Na-U-O system; dashed lines are the writer's extrapolations for equilibria involving the solid compounds. Also shown are the $\Delta \bar{F}_{O_2}^0$ values equivalent to those for out-of-reactor CO pressures calculated from Eq. (7.1) for a ThO_2 particle with a void/kernel ratio of 0.5.

However, an interaction of uranium with yttrium and rare-earth (RE) elements that promote the uranium valence to >4 is generally recognized to occur. It is widely known that individual oxides of RE elements and yttrium exist in extensive CaF_2 -type solid solutions with UO_2 and ThO_2 at HTGR temperatures; these solutions contain as much as ~ 75 mole % of $(\text{RE})\text{O}_{1.5}$. Similarly, CaF_2 -type solid solutions of $(\text{RE})\text{O}_{1.5}$ - Pa_2O_5 are reported.¹² Thus, at this point we now have an oxide solid solution containing all the actinide, yttrium, and RE elements. In this solid solution uranium exists at a valence higher than $4+$ at oxygen potentials significantly more negative than those in the pure UO_{2+x} system. Markin and Crouch¹³ have briefly investigated the U-Ce-O system at 800 to 950°C, and some of their data are plotted in Fig. 7.5; the extrapolation of $\Delta \bar{F}_{O_2}^0$ is based on $\Delta \bar{S}_{O_2}^0 \approx -30 \text{ cal mole}^{-1} (\text{°K})^{-1}$. A significant and extensive study of the U-Nd-O system at 850°C has been reported by Wadier,¹⁴ and part of his results are reproduced in Fig. 7.6. (Neodymium is the most abundant RE fission product.) Wadier¹⁴ also reported $\Delta \bar{S}_{O_2}^0 \approx -50 \text{ cal mole}^{-1} (\text{°K})^{-1}$ for $\text{O}/(\text{Nd} + \text{U})$ ratios of interest here. In addition, the O/U ratios shown in Fig. 7.6 were calculated by assuming a constant neodymium valence of $3+$; this approach demonstrates the significant effect of the U-RE interaction on promoting the uranium valence

above 4+. Leitnaker¹⁵ has reported the existence of $\text{U}_{0.6}\text{Eu}_{0.4}\text{O}_{1.95}$ at 900°C and at a CO/CO_2 ratio of 10; these data are shown in Fig. 7.6 and coincide exactly with Wadier's results. Stadlbauer et al.¹⁶ have investigated the $\text{U}_{0.95}\text{La}_{0.05}\text{O}_{2+x}$ system from 600 to 1000°C , and their results at 850°C are also shown in Fig. 7.6. Hagemark and Broli¹⁷ have made similar investigations in the U-La-O and U-Y-O systems at $1000 \leq T \leq 1400^\circ\text{C}$ and up to 5% of yttrium or lanthanum. Their results agree closely with those of Stadlbauer et al.¹⁶ No other oxygen potential data for any actinide-RE-O system have appeared in the literature—a rather abominable situation when one considers the importance of precise knowledge of oxygen release data upon fuel-containment interactions in the HTGR oxide fuel system as well as in the LWR and LMFBF oxide fuel systems. It is also clear that the data for ternary systems discussed above will be further influenced by mutual interactions between U, Pa, Y, La, and the RE elements, particularly cerium. Cerium is the only RE element that can be oxidized above 3+ valence at HTGR particle conditions; comparison of the U-Ce-O and U-Nd-O data indicates a quite dissimilar effect on the uranium valence.

Now consider the fission products Zr, Sr, Ba, and Mo. The zirconium exists as the dioxide, and the strontium and barium exist as the monoxide. Although phase diagrams indicate that the three phases present should be actinide oxide (with most of the Y, La, and RE in solution) plus ZrO_2 (RE-stabilized cubic structure?) plus the perovskite-type compound $\text{ZrO}_2 \cdot \text{Ba}_{1-x}\text{Sr}_x\text{O}$, strontium and barium are reported to exist simultaneously in association with zirconium as well as separately in irradiated fuels.¹⁸⁻²¹ This separation of strontium or barium brings up the possibility of interaction with molybdenum to form (Sr,Ba)-Mo-O compounds. McCarthy and Gooden²² have published the Sr-Mo-O phase diagram at 1200° C, and thermodynamic data for this and the analogous Ba-W-O system²³

would indicate that the compound $3\text{Sr}_{1-x}\text{Ba}_x\text{O} \cdot \text{MoO}_3$ may exist in an equilibrium of the type $3\text{SrO} + \text{Mo} + 1.5\text{O}_2 \rightarrow 3\text{SrO} \cdot \text{MoO}_3$ at oxygen potentials of interest here. However, such an Sr-Ba-Mo association has not been reported from microprobe analysis of irradiated fuels. It appears that the reason for this is that the reaction $3\text{SrO} \cdot \text{MoO}_3 + 3\text{ZrO}_2 \rightarrow 3[\text{SrO} \cdot \text{ZrO}_2] + \text{MoO}_2 + \frac{1}{2}\text{O}_2$ would occur at oxygen potentials found in HTGR particles. We further assume that molybdenum oxidizes only at the MoO_2 - Mo - O_2 equilibrium shown in Fig. 7.5.

Consider, finally, cesium and rubidium in the presence of UO_2 . Here, information on the cesium and rubidium systems will generally need to be deduced from analogous sodium systems. Battles et al.²⁴ and Blackburn²⁵ have published the equilibrium diagram shown in Fig. 7.7—the oxygen potential values at 1200°K for the equilibrium $\text{UO}_2 + 3\text{Na(l)} + \text{O}_2 \rightarrow \text{Na}_3\text{UO}_4$, $\Delta\bar{H}_{f,298}^0 = -477.7$ kcal/mole, and $\bar{S}_{298}^0 = 47.4$ cal mole⁻¹ (°K)⁻¹. Readily available $\bar{S}_{298}^0$ data for the other three components for this equilibrium lead to $\Delta\bar{S}_{298}^0 = -57$ cal mole⁻¹ (°K)⁻¹, used to extrapolate from Blackburn's 1200°K value in Fig. 7.5. Blackburn²⁵ next indicated the equilibrium $4\text{UO}_2 + 2\text{Na}_3\text{UO}_4 + \text{O}_2 \rightarrow 6\text{NaUO}_3$ at 1200°K. O'Hare and Hoekstra²⁶ estimate $\bar{S}_{298}^0 = 30.1$ cal mole⁻¹ (°K)⁻¹ for NaUO_3 , which leads to $\Delta\bar{S}_{298}^0 = -38.2$ cal mole⁻¹ (°K)⁻¹ for this equilibrium and the extrapolated behavior shown in Fig. 7.5. At more positive oxygen potentials, UO_2 and NaUO_3 are the stable phases for all HT particle conditions. It should be noted, however, that the melting and decomposition temperatures of these Na-U-O compounds are not known, and the extrapolations are only for the solid phases.

Fig. 7.7. The Na-U-O equilibrium diagram at 800°C. Also shown as the shaded area is the composition range for the (Cs + Rb)-U-O system existing in the coated particles studied here.

The comparison of the Na-U-O and Cs-U-O systems assumes that analogous phase equilibria exist. The values of $\Delta\bar{F}_T^0$ for equilibria in the Cs-U-O system can be approximated very closely by use of the equation $\Delta\bar{F}_T^0 = \Delta\bar{H}_{f,298}^0 - T \Delta\bar{S}_{298}^0$, and, in fact, $\Delta\bar{S}_{298}^0$ can be assumed to be constant for the analogous Cs-U-O equilibria. Therefore, the only difference in $\Delta\bar{F}_T^0$ for the two systems will originate in $\Delta\bar{H}_{f,298}^0$ differences. The only direct comparison available is for M_2UO_4 ; for $M = Na$, $\Delta\bar{H}_{f,298}^0 = -445.6$ kcal/mole;²⁷ for $M = Cs$, $\Delta\bar{H}_{f,298}^0 = -453.5$ kcal/mole.²⁸ Readily available $\Delta\bar{H}_{f,298}^0$ data²⁹ for M_2O , MBr , M_2CO_3 , MCl , $MClO_4$, MI , MNO_3 , MOH , M_2S , and M_2SO_4 indicate that $\Delta\bar{H}_{f,298}^0$ for the cesium compound averages 4 kcal/mole more negative than that for the sodium. Thus, the oxygen potentials for the Cs-U-O system may be slightly more negative than those shown for the Na-U-O system in Fig. 7.5. The rubidium system will be assumed to behave identically to the cesium system. Interactions of the Cs-Th-O system have not been studied and thus will not be considered here; only a limited amount of information on the alkali-metal-Pa-O systems exists, and at oxygen potentials more positive than those of interest here. Having performed this exercise, we will assume that cesium and rubidium oxides are not stable at temperatures used in the measurements of gas pressures on particles from HT-12 through -15. This assumption is based primarily on the lack of evidence of the stability of these compounds above 1200°K. Conversely, they should be present below 1200°K and not only combine cesium into a compound, with a significantly lower overpressure of Cs, but also they would combine with oxygen and lower the oxygen release per fission. At a Cs + Rb yield for ^{233}U of 0.187 per fission, this additional combined oxygen would be 0.126 O/f as $(Rb_{1-z}Cs_z)_3UO_4$ and 0.187 O/f as $Rb_{1-z}Cs_zUO_3$.

7.5 Interpretation of Oxygen Release Data

At this point a comparison is possible of the measured and theoretical oxygen release per fission. First, it is recognized that the 27-day ^{233}Pa had decayed to ^{233}U by the time the gas pressure measurements were made on the HT particles. The total out-of-reactor uranium concentration is thus the sum of the in-reactor ^{233}Pa and uranium, as shown in Fig. 7.4. Second, Eq. (7.1) was used to calculate the in-particle oxygen potential values shown in Fig. 7.5 for a particle having a void volume equal to one-half of the kernel volume. The calculations at 5% FIMA in Table 7.3 can then be considered. The ratios of $(Y + RE-Ce)/U$, Ce/U , and $U/\text{fission}$ were obtained from Fig. 7.4; here cerium is considered separately from the rest of the RE elements so that the data for the Ce-U-O system in Fig. 7.5 can be used. The oxygen potentials in Table 7.3 at 5% FIMA and at 1400, 1800, and 2200°K were obtained from Fig. 7.5. The maximum theoretical oxygen release per fission for ^{233}U fission in a thermal flux has been given as 0.264 O/f (see ref. 11, Table I); to this is added 0.07 for cerium existing as $CeO_{1.5}$ instead of the CeO_2 assumed in ref. 11. (^{144}Ce has decayed to insignificance; only ^{140}Ce and ^{142}Ce are chemically significant.) The combined oxygen resulting from the estimated temperature dependence of hyperstoichiometry, y , in the $CeO_{1.5+y}UO_2$ system (Fig. 7.5) is calculated in Table 7.3. (Assigning all the hyperstoichiometry to a change in cerium valence is used as a calculational convenience; the thermodynamic behavior probably involves hyperstoichiometry in both $CeO_{1.5+y}$ and UO_{2+x} .) Finally, the hyperstoichiometry in UO_{2+x} as a result of the U-(Y + RE, less Ce) interaction is obtained from Fig. 7.6 for the given oxygen potential and composition. The calculated O/f is thus 0.334 minus the combined hyperstoichiometric oxygen; this is compared with the measured O/f on the bottom two lines of Table 7.3. Similar calculations were made at 15% FIMA (Table 7.4). In both cases the agreement is reasonable. Other factors contributing to the observed disagreement, which are to be assessed in our ongoing studies, are effects of possible Sr + Ba loss from the kernel, and the errors in Q , Eq. (7.1), mentioned earlier as possibly resulting from errors in the 1700 to 2000°C experimental determinations of CO contents. One must also realize that the thermodynamic behavior of the Y-RE-U-O systems was extrapolated by as much as 1075°C on the basis of $\Delta\bar{S}_{O_2}^0$ values that are not well established.

Table 7.3. Out-of-reactor (HFIR) oxygen release per fission at 5% FIMA

(Y + RE-Ce)/U = 2.1/7.0 (77% U)			
Ce/U = 0.9/7.0 (12.5% Ce)			
U present/fission = 7.0/5.0 = 1.40 U/f			
Temperature (°K)	1400	1800	2200
$RT \ln P_{O_2}$ (kcal/mole) ^a	-97	-102	-105
Maximum theoretical O/f	0.334	0.334	0.334
Less combined oxygen			
y moles O as CeO _{1.5+y} at:			
y = 0.5; $0.5 \times \frac{0.9 \text{ Ce}}{5 \text{ fissions}}$	0.09		
y = 0.3		0.054	
y = 0.1			0.018
x moles O as UO _{2+x} at:			
x = 0.14; 0.14×1.40	0.196		
x = 0.12		0.168	
x = 0.10			0.14
Calculated O/f released	0.039	0.112	0.176
Actual O/f ^b	0.031	0.074	0.129

^aSee Fig. 7.5.

^bSee Eq. (7.1).

Table 7.4. Out-of-reactor (HFIR) oxygen release per fission at 15% FIMA

(Y + RE-Ce)/U = 6.2/7.8 (56% U)			
Ce/U = 2.6/7.8 (25% Ce)			
U present/fission = 7.8/1.5 = 0.52 U/f			
Temperature (°K)	1400	1800	2200
$RT \ln P_{O_2}$ (kcal/mole) ^a	-87	-87	-87
Maximum theoretical O/f	0.334	0.334	0.334
Less combined oxygen			
y moles O as CeO _{1.5+y} at:			
y = 0.5; $0.5 \times \frac{2.6 \text{ Ce}}{15 \text{ fissions}}$	0.087		
y = 0.45		0.078	
y = 0.2			0.035
x moles O as UO _{2+x} at:			
x = 0.24; 0.24×0.52	0.125		
x = 0.19		0.099	
x = 0.14			0.073
Calculated O/f released	0.122	0.157	0.246
Actual O/f ^b	0.084	0.20	0.35

^aSee Fig. 7.5.

^bSee Eq. (7.1).

It is also important to note that the in-reactor oxygen release in the HFIR must be considerably different from that measured out-of-reactor. This results primarily from the presence of $^{233}\text{PaO}_{2+z}$. Table 7.5 gives the results of these calculations, which are analogous to those used for Tables 7.3 and 7.4 and were performed so that O/f , P_{CO} , and $RT \ln P_{\text{O}_2}$ were mutually consistent. Comparison of the calculated O/f values in Tables 7.3 and 7.4 indicates that significantly less oxygen is released in the HFIR at $\leq 1800^\circ\text{K}$. Thus, prediction of in-reactor oxygen release for fission in ThO_2 particles must be based on a reasonably precise knowledge of the time-dependent protactinium and uranium concentrations in a particular reactor environment.

The oxygen release per fission for ThO_2 in an HTGR can also be estimated. The ^{233}Pa and total uranium contents were calculated⁸ for typical HTGR conditions and are also shown in Fig. 7.4. Here it can be seen that the in-HTGR uranium concentration is ~ 0.5 of the out-of-HFIR uranium concentration, whereas the ^{233}Pa concentration is insignificant for the mass-balance calculations. Thus, since significantly less uranium is available in the HTGR ThO_2 particles to form UO_{2+x} , the O/f is increased to values higher than those calculated from Eq. (7.1). Calculations similar to those in Tables 7.3 and 7.5 for HTGR burnup conditions at 5% FIMA lead to the oxygen potential and P_{CO} values shown in Fig. 7.8.

Table 7.5. Estimated in-reactor oxygen released per fission at 5% FIMA during HFIR irradiation

$(Y + \text{RE-Ce})/\text{U} = 1.7/3.0$ (64% U) ^a			
$\text{Ce}/\text{U} = 1.2/3.0$ (29% Ce) ^a			
$\text{U present/fission} = 3/5 = 0.6 \text{ U}/f$			
$\text{Pa present/fission} = 4/5 = 0.80 \text{ Pa}/f$			
Temperature ($^\circ\text{K}$)	1400	1800	2200
$RT \ln P_{\text{O}_2}$ (kcal/mole) ^b	-114	-105	-102
Maximum theoretical O/f	0.344 ^a	0.344 ^a	0.344 ^a
Less combined oxygen			
z moles O as PaO_{2+z} at			
$z = 0.21, 0.21 \times 0.8$	0.168		
$z = 0.15$		0.12	
$z = 0.05$			0.040
y moles O as $\text{CeO}_{1.5+y}$ at			
$y = 0.30, 0.30 \times \frac{1.2 \text{ Ce}}{5 \text{ fissions}}$	0.072		
$y = 0.3$		0.072	
$y = 0.1$			0.024
x moles O as UO_{2+x} at			
$x = 0.17 \times 0.6$	0.102		
$x = 0.16$		0.096	
$x = 0.11$			0.066
Calculated O/f released	~ 0.002	~ 0.056	~ 0.22

^aThe in-reactor cerium contents now include the 4.7% yield of ^{144}Ce instead of the RE-daughter ^{144}Nd , the mass-balance calculations reflect this change.

^bSee Fig. 7.5

Fig. 7.8. Calculated oxygen potential and P_{CO} values in ThO_2 particles at 5% FIMA for three different conditions: during irradiation in the HT position, after HT exposure and 1.5 to 2 years of cooling, and during irradiation in the HTGR. The assumed void volume is 0.5 of the buffer volume

References

1. T. B. Lindemer and R. L. Pearson, "Apparatus for Measuring Gases from Irradiated Fuel Particles," *J. Nucl. Mater.* **55**, 359-61 (1975).
2. G. W. Horsley, AERE, Harwell, private communication, March 1975.
3. D. J. Clough, G. W. Horsley, J. W. McMillan, B. E. Sheldon, B. L. Taylor, G. J. Weldrick, and J. Williams, "The Determination of Gases in Coated Particle and Ceramic Fuels," *Post-Irradiation Examination Techniques, Proc. Conf. U. of Reading, 1972*, British Nuclear Energy Society—Institute of Civil Engineers, London, 1972.
4. H. Bildstein and H. Strigl, "Determination of Free Volumes and Gas Content of Coated Fuel Particles for Gas-Cooled Reactors," *Post-Irradiation Examination Techniques, Proc. Conf. U. of Reading, 1972*, British Nuclear Energy Society—Institute of Civil Engineers, London, 1972.

5. H. T. Kerr, ORNL, private communication, January 1976.
6. E. J. Allen, *CACA-2: Revised Version of CACA—A Heavy Isotope and Fission-Product Concentration Calculational Code for Experimental Irradiation Capsules*, ORNL/TM-5266 (February 1976).
7. W. Knoch and S. Schieferdecker, Tagungsbericht der 3., Paper No. 10, Internationalen Protaktiniumkonferenz (Schloss Elmau bei Mittenwald, April 1969), H.-J. Born Institut für Radiochemie der Technischen, Universität München (1971).
8. L. E. J. Roberts and A. J. Walker, "The Oxides of Protactinium," pp. 51–59 in *Physico-Chimie der Protactinium*, vol. 154, Colloques Internationaux du Centre National de la Recherche Scientifique, Paris, 1966.
9. T. B. Lindemer and H. J. de Nordwall, *An Analysis of Chemical Failure of UO₂ and Other Oxide Fuels in the High-Temperature Gas-Cooled Reactor*, ORNL-4926, pp. 6–11 (January 1974).
10. K. Hagemark and M. Broli, "Equilibrium Oxygen Pressures Over the Nonstoichiometric Uranium Oxides UO_{2+x} and U₃O_{8-z} at Higher Temperatures," *J. Inorg. Nucl. Chem.* **28**, 2837–50 (1966).
11. S. Aronson and J. C. Clayton, "Thermodynamic Properties of Nonstoichiometric Urania-Thoria Solid Solutions," *J. Chem. Phys.* **32**, 749–54 (1960).
12. C. Keller, "On the Solid-State Chemistry of Protactinium Oxides," pp. 73–79 in *Physico-Chimie du Protactinium*, vol. 154, Colloques Internationaux du Centre National de la Recherche Scientifique, Paris 1966.
13. T. L. Markin and E. C. Crouch, "Thermodynamic Data for U-Ce-Oxides," *J. Inorg. Nucl. Chem.* **32**, 77–82 (1970).
14. J. F. Wadier, *Phase Diagram and Thermodynamic Properties of the Uranium-Neodymium-Oxygen System*, CER-R-4507, p. 59 (November 1973).
15. J. M. Leitnaker, "Applications of Thermodynamics for Predicting and Understanding the Performance of Fast Breeder Reactor Oxide Fuels," *J. Nucl. Mater.* **51**, 95–105 (1974).
16. E. Stadlbauer, U. Wichmann, U. Lott, and C. Keller, "Thermodynamics and Phase Relationships of the Ternary Lanthanum-Uranium-Oxygen System," *J. Solid State Chem.* **10**, 341–50 (1974).
17. K. Hagemark and M. Broli, "Equilibrium Oxygen Pressures Over Solid Solutions of Urania-Yttria and Urania-Lanthana at 1100 to 1400°C," *J. Am. Ceram. Soc.* **50**, 563 (1967).
18. C. A. Friskney and K. A. Simpson, "The Behavior of Fission-Product Barium and Strontium in Irradiated UO₂," *J. Nucl. Mater.* **57**, 121–22 (1975).
19. M. Koizumi, M. Satoh, and K. Noro, "Phase Study on Solid Fission Products Ba, Sr, and Zr in Oxide Fuel," *J. Nucl. Mater.* **51**, 90–94 (1974).
20. L. Carlsson, "Non-Elastic Mechanical Behavior in SrOZrO₃ by Reorientation," *J. Mater. Sci.* **5**, 325–39 (1970).
21. C. E. Johnson, I. Johnson, P. E. Blackburn, and C. E. Crouthamel, "Effects of Oxygen Concentration on Properties of Fast Reactor Mixed-Oxide Fuel," *React. Technol.* **15**, 303–38 (1973).
22. G. J. McCarthy and C. E. Gooden, "Compound Formation in the System Sr-Mo-O," *J. Inorg. Nucl. Chem.* **35**, 2669–72 (1973).
23. V. B. Parker, D. D. Wagman, and W. H. Evans, *Selected Values of Chemical Thermodynamic Properties, Tables for the Alkaline-Earth Elements*, NBS Tech. Note 270-6, U.S. Government Printing Office, Washington, D.C., 1971.
24. J. E. Battles, W. A. Shinn, and P. E. Blackburn, "Thermodynamic Investigation of Trisodium Uranium(V) Oxide (Na₂UO₄) IV, Mass Spectrometric Study of the Na + U + O System," *J. Chem. Thermodyn.* **4**, 425–39 (1972).

25. P. E. Blackburn, "Reaction of Sodium with Uranium-Plutonium Oxide and Uranium Oxide Fuels," pp. 393-410 in *Behavior and Chemical State of Irradiated Ceramic Fuels, Proc. Panel, Vienna, August 1972*, IAEA, Vienna, 1974.

26. P. A. G. O'Hare and H. R. Hoekstra, "Thermochemistry of Uranium Compounds IV. Standard Enthalpy of Formation of Sodium Uranium(V) Trioxide (NaUO_3)," *J. Chem. Thermodyn.* **6**, 965-72 (1974).

27. P. A. G. O'Hare and H. R. Hoekstra, "Thermochemistry of Uranium Compounds II. Standard Enthalpy of Formation of -Sodium Uranate ($-\text{Na}_2\text{UO}_4$)," *J. Chem. Thermodyn.* **5**, 769-75 (1973).

28. P. A. G. O'Hare and H. R. Hoekstra, "Thermochemistry of Uranium Compounds III. Standard Enthalpy of Formation of Cesium Uranate (Cs_2UO_4)," *J. Chem. Thermodyn.* **5**, 251-58 (1974).

29. R. C. Weast, *Handbook of Chemistry and Physics*, 53rd ed., pp. D-64, D-69, D-70, The Chemical Rubber Co., Cleveland, Ohio, 1972.

8. FAILURE DETERMINATION

This experiment was designed to confirm particle failure predictions and thereby establish minimal engineering coating design criteria rather than to demonstrate the ability of coated particles to successfully withstand reactor environments as in previous HFIR target capsules. To meet this objective it was necessary to determine, with certainty, whether a particular coating design survived or failed during irradiation. A further requirement is then to be able to establish failure determination procedures that are not ambiguous. At the time this experiment was planned, it was thought that the survivability of the Biso-coated ThO₂ particles could be determined by postirradiation visual inspection alone. However, the results of gas pressure measurements described in Sect. 7.2 revealed the absence of fission gas in several coated particles reported intact by postirradiation visual examination; therefore, a more thorough study of coating failures was initiated. These studies compared the results of visual inspection, gas pressure measurements, hot chlorine leaching, and electron microscope examinations.

8.1 Visual Inspection

The results of the postirradiation visual inspection were reported in Sect. 4.1 and listed in Table 4.1. These results indicated that three ORNL coating designs, OR-1838, OR-1840, and OR-1849, performed with few or no visible failures in capsules HT-12 through HT-15 with the exception of OR-1840 in HT-15. On this basis and on design considerations, coated particles from batches OR-1840 and OR-1849 were selected for extensive gas pressure and fission product release studies. Because of the disagreement between gas pressure measurements and visual inspections mentioned above, 6 to 16 coated particles from each of 13 irradiation holders containing coated particles from batches OR-1840 and OR-1849 were subjected to additional testing. These samples represented coated particles from each of the two batches irradiated at two temperatures and to four burnups, with three exceptions. There were insufficient coated particles available from two holders, and in one sample, OR-1840, 93% of the coatings had visibly failed. Prior to hot chlorine leaching, each coated particle was carefully reinspected under a stereomicroscope. This visual inspection agreed with the visual results obtained in the hot cells previously.

8.2 Hot Gaseous Chlorine Leaching¹ and Associated Studies

The samples of 6 to 16 coated particles were packaged in separate holes in porous graphite blocks to retain their individual identity and were leached with hot gaseous chlorine at $1000 \pm 100^{\circ}\text{C}$. Prechlorination of the empty sample holders had removed impurities from the graphite. Leaching was carried to a minimum of 17 hr if no thorium was collected. If thorium was collected initially, the leaching was continued in 20-hr steps until the accumulative thorium ceased to increase. The maximum total time required was 60 hr. This procedure ensured collection of the total thorium content of the defective particles. In all but two samples involving coating failures, the maximum amount of thorium was collected during the first leaching step. In the two where thorium increased during the second step, the initial porosity was probably small and increased as a result of reaction during leaching. Such a reaction occurs between the thorium oxide and carbon where chlorine penetrates through to the fuel kernel. The condensed fission products and metal chlorides were leached with a dilute acid solution from the combustion system after each gas leach period. Total thorium in the leach solution was determined by the arsenazo III method, and the fission products were determined by gamma-ray spectrometry. The coated particles were passed over an ion chamber as they were unloaded after leaching to determine failures

initially. In addition, most of the particles have been reanalyzed by gamma spectrometry to determine quantitatively the loss of fission products during leaching from each particle.

A comparison of the number of coating failures as determined by visual inspection, gas pressure measurements, and hot chlorine leaching is given in Table 8.1. The irradiation conditions are given also. The burnups given were determined from fission product inventories described in Sect. 6. Irradiation temperatures given were averaged over the irradiation period and, in the short irradiation capsule (HT-12), are about 100°C less than the maximum temperature. For the longer irradiation capsules the difference is not as great (see Appendix A). These results show that coating failures up to 100% (HT-15, holder 8), as indicated by gas pressure measurements and hot chlorine leach, were not discernable by visual examination. The results also show a fair agreement between the fraction of failures determined by particle activity measurements after leaching with that indicated by thorium collection during leaching. The thorium results, however, are low by 15 to 25%.

A comparison of the fraction of failures for each batch in the same irradiation capsule indicates that the highest number of failures occurred at the lower conditions of temperature, burnup, and fast fluence. This is illustrated in capsules HT-14 and -15 by comparing the failures in holder 8 with those in holder 21, and those in holder 13 with those in holder 26. A slight exception exists at lower burnups, where 1 out of 16 leached particles failed in capsule HT-12, holder 26.

In Table 8.2 the fraction of fission products collected during leaching is compared with the fraction of coating failures and the fraction of thorium collected. The fraction of fission products collected is based on the totals as analyzed in the particles before leaching. The ^{144}Ce and ^{137}Cs results agree more closely with the true failure fraction than do the ^{232}Th results, with the exception of one cesium analysis; however, the ^{232}Th results are more uniform.

The cesium and cerium losses during leaching from individual coated particles are presented in Tables 8.3 and 8.4 respectively. Post-leach analyses are still continuing, but these data represent most of the series, since analyses will not be performed on particles that were definitely shown to be defective.

The pre-leach analyses were performed on a different spectrometry system than were the post-leach analyses. Although standards were used for calibration, calibration errors still occurred. In most cases the pre-leach inventories averaged less for intact coated particles than did the post-leach inventories, and the assumption was made that our calibration procedure has improved with time. Therefore, earlier values were corrected using a constant factor to agree with the later results, with the exception of samples HT-12-21 and HT-12-26. The pre-leach analyses of these sets of particles were taken at a later date and were higher than the post-leach results. The average negative loss before correction is indicated in the tables as bias.

Three defective coated particles were analyzed after leaching. The cesium and cerium losses ranged from 98 to 100% in these particles. Of the intact coated particles, only particle 4 from HT-13-26 showed a loss of cesium and cerium outside the scatter of the data. This exception could be a possible indication of the beginning of a failure caused by chlorine penetration of an intact coating. It could also indicate that the coating was beginning to fail during irradiation, or it could be the result of an analytical error.

All of the coated particles that failed were inspected under the stereomicroscope after leaching to determine the type of failure, with the exception of those from holder HT-14-13 and the one particle failure in HT-12-26. Only three coatings were definitely cracked out of the 32 defective coated particles inspected. Three other coatings had holes in the surface after leaching. No other defects were visible. The holes were caused by a reaction involving the fuel, chlorine, and coatings. This would occur only if chlorine can penetrate the coating; this reaction can be suppressed by the addition of CO to the leach gas.

Table 8.1. Failures in Biso-coated ThO₂ particles from HT-12 through HT-15 capsules as determined by different methods

	Capsule			
	HT-12	HT-13	HT-14	HT-15
Holder 8, batch OR-1840, design^a 402-25-50				
Average temperature (°C)	1090	1190	1250	1260
Burnup (% FIMA)	1	3	7	10
Fast fluence ($nvt \times 10^{21}$, $E > 0.18$ MeV)	3	6	9	11
Failures				
Visual inspection (%) ^b	0	0	0	0
Gas pressure ^c (fraction ^d)	ND ^e	0/6	3/3	ND
Hot chlorine leach				
Failures by particle activity (%)	0	6	94	100
ThO ₂ collected (% of total)	0	5	80	76
Number of particles leached	16	16	16	6
Holder 21, batch OR-1840, design^a 402-25-50				
Average temperature (°C)	1370	1460	1500	1500
Burnup (% FIMA)	1	6	13	16
Fast fluence ($nvt \times 10^{21}$, $E > 0.18$ MeV)	4	8	14	16
Failures				
Visual inspection (%) ^b	0	0	0	93
Gas pressure ^c (fraction ^d)	ND	0/10	3/8	ND
Hot chlorine leach				
Failures by particle activity (%)	0	0	19	ND
ThO ₂ collected (% of total)	0	0	14	ND
Number of particles leached	16	16	16	0
Holder 13, batch OR-1849, design^a 508-79-75				
Average temperature (°C)	1180	1270	1320	1330
Burnup (% FIMA)	1	5	9	11
Fast fluence ($nvt \times 10^{21}$, $E > 0.18$ MeV)	3	7	11	13
Failures				
Visual inspection (%) ^b	0	0	0	0
Gas pressure ^c (fraction ^d)	ND	ND	2-3/6	2/3
Hot chlorine leach				
Failures by particle activity (%)	0	0	75	88
ThO ₂ collected (% of total)	0.3	0	58	70
Number of particles leached	16	12	8	8
Holder 26, batch OR-1849, design^a 508-79-75				
Average temperature (°C)	1450	1520	1550	1550
Burnup (% FIMA)	1	6	14	16
Fast fluence ($nvt \times 10^{21}$, $E > 0.18$ MeV)	4	9	14	16
Failures				
Visual inspection (%) ^b	0	0	0	3
Gas pressure ^c (fraction ^d)	0/3	0/6	0/5	0/5
Hot chlorine leach				
Failures by particle activity (%)	6	0	ND	0
ThO ₂ collected (% of total)	5	0	ND	0
Number of particles leached	16	16	0	8

^aDesign gives kernel diameter, buffer thickness, and outer coating thickness, all dimensions are in microns

^bSample size of 50 to 75 coated particles

^cFailures determined by absence of fission gas during pressure measurements

^dThe denominators of fractions used in the table are the numbers of particles inspected

^eND – not determined

Table 8.2. Fission products and thorium collected during chlorine leaching at 1000°C
[fraction of total (%)]

Sample	Number of particles	^{106}Ru	^{125}Sb	^{137}Cs	^{144}Ce	^{232}Th	Number of particles failed	Failures (%)
HT-12-8	16	≤ 0.02	≤ 0.01	≤ 0.004	≤ 0.002	< 0.02	0/16	0.0
HT-12-13	16	ND ^a	0.18	0.040	0.028	0.33	0/16	0.0
HT-12-21	16	0.24	0.097	0.015	0.32	< 0.02	0/16	0.0
HT-12-26	16	4.8	ND	5.2	4.8	4.8	1/16	6.2
HT-13-8	16	5.9	ND	5.2	5.5	4.9	1/16	6.2
HT-13-13	12	ND	ND	0.007	0.002	< 0.014	0/16	0.0
HT-13-21	16	≤ 0.011	≤ 0.022	0.037	0.005	0.021	0/16	0.0
HT-13-26	16	0.035	0.060	0.004	0.014	< 0.01	0/16	0.0
HT-14-8	16	110	ND	82	103	80	15/16	93.8
HT-14-13	8	57	ND	62	76	58	6/8	75.0
HT-14-21	16	16	≤ 14	6.9	17	14	3/16	18.8
HT-14-26	0							
HT-15-8	6	106	81	109	114	76	6/6	100.0
HT-15-13	8	28	≤ 40	77	95	70	7/8	87.5
HT-15-21	0							
HT-15-26	8	0.32	2.4	3.1	0.085	< 0.047	0/8	0.0

^aNot determined.

Table 8.3. Cesium loss during chlorine leaching at 1000°C (%)

Particle	HT-12-8	HT-12-13	HT-12-21	HT-12-26	HT-13-8	HT-13-13	HT-13-26	HT-14-21
1	ND ^a	+1	0	0	+2	-2	0	+2
2	-4	-3	+1	+2	-1	+3	+2	0
3	-3	0	+2	+99	-12	0	0	+2
4	+1	0	-1	-3	+3	+1	+7 ^b	-2
5	+2	+1	+1	+1	+2	+2	+1	ND
6	-8	-2	+1	+1	+2	-1	+1	-2
7	+3	+1	+3	+4	+1	0	-1	-1
8	-2	+1	+6	+2	-3	-4	+1	+3
9	+1	+2	+1	+2	+3	0	0	+99
10	+2	+2	+3	-2	-1	0	-1	+98
11	-1	+3	+3	+1	-2	2	-2	ND
12	+4	+2	+2	+2	ND	1	+1	-1
13	-1	-7	+2	0	+2		+1	-2
14	+1	0	+3	+1	+2		0	+1
15	+3	-1	+2	-6	+1		0	-1
16	+2	+1	+1	-3	+1		-1	+1
Av. loss ^c	0	0	1	0	0	0	0	0
Bias ^d	0	-2	0	0	-4	-4	-4	-3

^aNot determined.

^bThis particle may have begun to fail. Data were not used in averages.

^cData from intact coated particles only.

^dOriginal inventories averaged less than final inventories because of spectrometer calibration errors. Original inventories were corrected for these amounts.

Table 8.4. Cerium loss during chlorine leaching at 1000°C (%)

Particle	HT-12-8	HT-12-13	HT-12-21	HT-12-26	HT-13-8	HT-13-13	HT-13-26	HT-14-21
1	ND ^a	+3	+1	+3	+4	-4	-2	+2
2	-3	-6	+8	+2	-8	+1	-11	-2
3	-1	+1	-2	+98	-10	-1	+13	+5
4	-1	+3	-2	+1	-1	+4	+21 ^b	-3
5	+5	+5	+5	-4	+3	-2	-2	ND
6	-3	-6	-2	+1	-1	+4	+6	-4
7	+1	+3	+1	+6	+1	0	-3	+4
8	-4	0	+5	0	-5	-5	+8	-2
9	+1	+4	+5	-2	+5	+3	-3	+100
10	-6	-1	+7	+6	-9	-5	+7	+99
11	-5	+2	+8	+5	+3	+2	-4	-2
12	+3	+3	-1	+6	ND	+3	-3	-2
13	+3	-3	+5	-1	+4		-1	+2
14	+4	0	+2	+2	+4		-1	0
15	+6	-11	+4	-5	+9		-3	-1
16	0	+5	+5	-1	0		-2	+3
Av. loss ^c	0	0	+3	+1	0	0	0	0
Bias ^d	-2	-4	0	0	-6	-6	-2	-4

^aNot determined.^bThis particle may have begun to fail. Data were not used in averages.^cData from intact coated particles only.^dOriginal inventories averaged less than final inventories because of spectrometer calibration errors. Original inventories were corrected for these amounts.

8.3 Scanning Electron Microscope Studies

Several defective coated particles were examined under the scanning electron microscope (SEM). Scanning electron micrographs of coatings from HT-15-21, batch OR-1840, of which 93% failed by visual inspection, are shown in Figs. 8.1 and 8.2. Apparently, fragments of fuel from adjacent failed particles had reacted with the coating of the particle shown in Fig. 8.1. Figure 8.1*b* is an enlargement of some of the fragments embedded in the coating. The enlargement of another area of the same coating in Fig. 8.1*c* shows an apparent surface porosity and a fibrous structure. It is uncertain whether the particle shown in Fig. 8.2 has a coating or not. The cracks seen in the enlarged view in Fig. 8.2*c* might indicate melting during irradiation.

Micrographs of defective coated particles from holder HT-14-21 are shown in Figs. 8.3, 8.4, and 8.5. Figure 8.3 is a comparison of micrographs from an unleached coated particle, on the left, with a leached coated particle on the right. The surface porosity in the unleached coating is larger than in the leached coating. However, these micrographs may not be typical of other coated particles, even in the same holder. The hole in the leached coated particle is shown in more detail in Fig. 8.4. The hole was caused by a reaction between the fuel, chlorine, and pyrocarbon. The pits adjacent to the hole may be the results of the same reaction if bits of fuel were ejected during chlorination. This coating was broken under pressure to obtain the cross-section views in Fig. 8.4*b* and 8.4*d*. Views of the cross section of the same coating at a location opposite the hole are shown in Fig. 8.5. Note that the porous, fibrous structure at the coating surface is only a few microns in depth. In the enlargement at 10,000X in Fig. 8.5*d*, concentric-spherical growth features are seen interspaced among a somewhat layered structure.

A comparison between leached coated particles, one of which survived and the other failed, is shown in Fig. 8.6. The apparent surface porosity seen in the coatings in Figs. 8.1, 8.3, 8.4, and 8.5 is absent in these coatings. No distinct difference is shown between the coating that survived and the one that failed.

Fig. 8.1. Scanning electron micrographs of Biso-coated ThO_2 particles from HT-15-21, batch OR-1840, irradiation temperature 1550°C , burnup 20% FIMA. 93% gross failures. Coated particles were not leached. Shows interaction of coating with fragments of fuel, also the porosity and fibrous structure of the coating surface. (a) Overall view, $100\times$; (b) embedded fragments, $2000\times$; (c) coating surface, $500\times$; (d) coating surface, $2000\times$.

Fig. 8.2. Scanning electron micrographs of Biso-coated ThO_2 particles from HT-15-21, batch OR-1840, irradiation temperature 1550°C , burnup 20% FIMA. 93% gross failures. Coated particles were not leached: Shows grossly deformed particles with fuel or coating fragments attached to surface. One area appears to have been molten. (a) Overall view, 100X; (b) fragments to surface, 250X; (c) surface at 500X; (d) molten area, 2000X.

Fig. 8.3. Scanning electron micrographs of Biso-coated ThO_2 particles from HT-14-21, batch OR-1840, irradiation temperature 1530°C , burnup 16% FIMA. 19% failed. Compares surface of unleached coated particle with that of particle leached in chlorine at 1000°C . (a) Overall view of unleached particle, $100\times$; (b) overall view of leached particle, $100\times$; (c) surface of unleached particle, $1000\times$; (d) surface of leached particle, $1000\times$.

Fig. 8.4. Scanning electron micrographs of Biso-coated ThO_2 particle from HT-14-21, batch OR-1840, irradiation temperature 1530°C , burnup 16% FIMA. 19% failed. Shows hole in coating caused by fuel-chlorine-coating reaction during leaching. (a) View of hole and surface pitting, $300\times$; (b) cross section of hole and coating, $300\times$; (c) enlarged view of hole, $1000\times$; (d) enlarged cross-section view, $1000\times$.

Fig. 8.5. Scanning electron micrographs of Biso-coated ThO_2 particle from HT-14-21, batch OR-1840, irradiation temperature 1530°C , burnup 16% FIMA. 19% failed. Shows particle was leached. Shows variation in structure across fractured edge of coating. (a) View of fractured edge opposite hole shown in Fig. 8.4, 300X; (b) edge view, 1000X; (c) edge view, 3000X; (d) edge view, 10,000X.

Fig. 8.6. Scanning electron micrographs of Biso-coated particles from HT-13-26, batch OR-1849, irradiation temperature 1490°C, burnup 8% FIMA. None failed. Also from HT-15-8, batch OR-1840, irradiation temperature 1280°C, burnup 15% FIMA. 100% failed. Both particles were leached. Compares surfaces of permeable or defective coating with one which remained impermeable. (a) Overall view of particle with impermeable coating, 100X; (b) overall view of defective coated particle, 100X; (c) view of impermeable coating surface, 3000X; (d) view of defective coating surface, 3000X.

Micrographs of unirradiated, unleached, and leached coated particles were also taken to determine the effects of irradiation and leaching on the surface appearance. These are presented in Fig. 8.7; the unleached coatings are shown on the left, and the leached coatings are on the right. No difference can be found either in the surface or cross-section views of the coatings as a result of leaching. The granular appearance of the surfaces of unirradiated coatings is quite different from that of irradiated coated particles shown in Figs. 8.1, 8.3, 8.4, and 8.6. The fractured surface appearance is also different; the unirradiated surfaces show spherical details but lack the distinct concentric rings shown in Fig. 8.5. This difference could be an artifact caused by differences in viewing angles.

8.4 Discussion of Results

The lack of any evidence of coating failure in either optical or scanning electron microscopy suggests that the permeability observed in some of the coatings in these experiments is due either to microcracks or porosity. Since no failures were detected by 1000°C gaseous chlorine leaching of unirradiated control particles, the failures in the irradiated coated particles must have occurred during irradiation.

Kaae,² using electron microscopy, has shown that internal cracks developed in unirradiated pyrocarbon deposited from propane at 1300°C during an anneal at 1900°C for 2 hr. The pyrocarbon had an as-coated density of 2.04 g/cm³, a crystallite size (L_c) of 33 Å, and a Bacon anisotropy factor (BAF) of 1.00. The cracks were of the same length as the largest pore size in the as coated material. Kaae³ also found that cracks developed in high-density propane-derived pyrocarbon irradiated to a fluence beyond 2×10^{21} nvt ($E > 0.18$ MeV). This pyrocarbon had an as-coated density of 2.04 g/cm³, a crystallite size of 33 Å, and a BAF of 1.30. After irradiation to a fast fluence of 7.7×10^{21} nvt at 1550 to 1600°C, the cracks were numerous both around the growth features of the pyrocarbon and within the growth features. It was suggested that the development of the cracks was responsible for the decrease in density observed above intermediate fluences. Kaae found no cracks either after annealing or irradiation in low-density pyrocarbon, and after the initial densification, the density remained nearly constant to a fast-neutron fluence of 8×10^{21} nvt.

The width of the largest cracks shown in the electron micrographs by Kaae appears to be up to several hundred angstroms. Since the ionic radii of Cl, Cs, Kr, Xe, and ThCl₄ are 1.8, 2.7, 1.9, 2.1, and 3.6 Å, respectively, a network of cracks and pores could serve to account for the permeability observed in these experiments in the lower-temperature samples. However, if microcracks became interconnected, one would expect the pyrocarbon strength to decrease, resulting eventually in explosive fragmentation due to the internal gas pressure in the coated particles. More coatings failed at the lower temperature (~1200°C) than at the higher temperature (~1500°C). The pyrocarbon densities in batches OR-1840 and OR-1849 were 2.01 and 1.99 g/cm³ respectively. Perhaps at the higher temperature, the increased creep rate served to accommodate dimensional change and to diminish crack formation. Pyrocarbons reacting with fuel, fission products, or external contaminants could result in porosity occurring during irradiation.

Regardless of the type of failure, the primary significance of these results is that the coatings developed permeability during irradiation which could not be detected visually. It is also doubtful that metallography would show such failures. Fission gas release during irradiation or annealing would detect this type of failure but could not distinguish permeability from pressure vessel failure. Since nearly all previous irradiation experiments have used visual inspection, metallography, or fission gas release for the detection of failures, and since fission gas release has been attributed to pressure vessel failure, the extent of failure due to the development of permeability during irradiation has not been assessed. All efforts in past coating development have been directed toward the design of coatings to withstand pressure vessel failure during

Fig. 8.7. Scanning electron micrographs of Biso-coated ThO_2 particles from batch OR-1849, as coated. Compares appearances of surface and fractured edge of coatings of unleached particles with those of particles leached in chlorine at 1000°C for 17 hr. (a) Surface of unleached coating, 10,000X; (b) surface of leached coating, 10,000X; (c) fractured edge of unleached coating, 10,000X; (d) fractured edge of leached coating, 10,000X.

irradiation. That research indicated that the coating density should be less than maximum for the coatings to survive the effects of fast-neutron damage.⁴ The coatings irradiated in this experiment were of a higher density (see Sect. 2.1). If the permeability observed here is the result of internal reactions or structural change, then the effect of coating characteristics on the development of irradiation-induced permeability must be considered.

The requirements for a coating that is resistant to the development of permeability may be similar to those necessary to prevent pressure vessel failure. However, these studies indicate that several coatings survived to approximately the design limits for HTGR fertile fuel. More research is necessary to verify whether irradiation-induced permeability is a problem and, if so, to define the optimum coating design to deter both pressure vessel failure and irradiation-induced permeability. Such studies should include the effects of a range of irradiation conditions.

These studies have also shown that visual inspection alone is insufficient to guarantee that coatings have not failed. The following discussion is directed toward methods of coating failure detection.

The visual inspection technique used in the post-irradiation examination (PIE) primarily detects cracked coatings. Microscopic defects are easily overlooked and submicroscopic defects would not be seen. At a magnification of 10,000 produced with the scanning electron, the width of cracks or pores necessary to pass gas atoms would be less than a micron, hardly visible, and difficult to interpret as well. Explosive failures often produce fragments small enough to mix with other debris, and these, too, cannot be quantitatively assessed by visual inspection.

The more rigorous investigations of gas measurements and hot gaseous chlorine leaching detect submicroscopic coating failures as well as gross failures. Gamma-counting the coated particles separately after leaching, as was done in these experiments, can increase the accuracy in failure determination. However, gas pressure measurements and gaseous chloride leaching also have limitations.

Gas pressure measurements described in Sect. 7.2 were carried out to investigate kernel chemistry. There is some question as to whether the heating of coated particles above their irradiation temperature may have caused additional failures. These experiments are performed on single coated particles, are expensive and tedious, and therefore not useful for routine failure detection. An alternate method of gas detection, cracking single coated particles at room temperature for the collection of fission gas, has been used.^{5,6}

The hot gaseous chlorine leaching procedure described previously is applicable only to Bisco-coated particles. The possibility also exists that hot chlorine leaching can cause damage to the coatings, creating additional failures, especially at temperatures higher than 1000°C. However, the results of these studies do not indicate that additional failures occurred. There were no failures found in the unirradiated control samples of 16 particles from each batch, and there were no failures observed in several irradiated samples. Also, no difference could be observed in the SEM micrographs of control and leached coatings up to magnifications of 10,000X.

A comparison of the failures detected by the two methods is given below:

Method	Fraction of coated particles failed (%)								
	Sample HT—								
	13-8	14-8	13-21	14-21	14-13	15-13	12-26	13-36	15-26
Gas pressure	0	100	0	38	50	67	0	0	0
Chlorine leach	6	94	0	19	75	88	6	0	0

Excess failures in the gas pressure method could be caused by the high temperatures used. It might be argued that excess failures in the chlorine leach values were caused by hot chlorine opening up porosity already developing in particles weakened by irradiation.

A method routinely used for quality control of unirradiated uncoated particles⁷ involves the determination of fission-gas release during the irradiation of samples of the coated particles for one-half hour at 1100°C. The release to birthrate for ^{85m}Kr (or other fission gases) is calculated and compared with that from similar coated-particle samples in which the coatings were precracked or laser drilled to predetermine a failure fraction. This method is applicable to loose-coated particles or fuel rods. There is some uncertainty regarding comparison of gas release from cracked loose-coated particles with that from particles with cracked coatings constrained in a matrix. Also, variations in kernel characteristics will influence the results.

An alternative to the procedures studied here is a new system being designed and fabricated to provide statistically accurate determinations of HTGR fuel particle performance.⁸ The system, known as the irradiated microsphere gamma analyzer (IMGA), has as one of its primary functions the capability to determine the failure fraction of irradiated fuel particles, that is, the fraction of fuel particles that have lost a significant amount of their fission products through defective or broken coatings. This determination is made possible by the different volatilities of fission products that emit easily detectable gamma rays. An example would be ⁹⁵Zr and ¹³⁷Cs. Because of the relatively low boiling point of cesium compared with zirconium (678°C and 4377°C respectively), cesium will diffuse or escape from a defective particle much more readily than zirconium in the high-temperature environment of an HTGR. Thus, a measurement of the ratio of ¹³⁷Cs activity to that of ⁹⁵Zr provides a direct measure of the particle's ability to retain fission products. An attractive feature of the ratio determination is its insensitivity to variation in the fuel particle design. It is anticipated that when IMGA is installed, it will be used to make all accurate failure fraction determinations.

If permeability is to be differentiated from pressure vessel failure, then visual inspection of loose or coated particles from deconsolidated fuel rods must be followed by a more positive method of failure detection of the apparently intact particles. Such determinations can be made by the hot gaseous chlorine leaching process or by the IMGA.

References

1. D. E. Lavalley, D. A. Costanzo, W. J. Lackey, and A. J. Caputo, *The Determination of the Defective Particle Fraction in HTGR Fuels*, ORNL/TM-5483, in publication.
2. J. L. Kaae, "The Effect of Annealing on the Microstructure and the Mechanical Properties of Poorly Crystalline Isotropic Pyrolytic Carbons," *Carbon* **10**, 691–99 (1972).
3. J. L. Kaae, "Irradiation-Induced Microstructural Changes in Isotropic Pyrolytic Carbons," *J. Nucl. Mater.* **57**(1), 82–92 (July 1975).
4. D. P. Harmon and C. B. Scott, *Development and Irradiation Performance of HTGR Fuel*, GA-A13173, General Atomic Company (Oct. 31, 1975).
5. P. Koss and H. Bildstein, *Testing and Evaluation of Reactor Fuel Particles*, Dragon Project Report 408 (January 1965).

6. M. T. Morgan, H. J. deNordwall, and R. L. Towns, *Release of Fission Products from Pyrocarbon-Coated HTGR Fuel Particles During Postirradiation Anneals*, ORNL/TM-4539 (December 1974).
7. R. D. Burnette, W. E. Bell, and H. L. Baldwin, "Fission Product Retention Characteristics of HTGR Fuel," *Nuclear Fuel Performance Conference, British Nuclear Energy Society, October 15-19, 1973, London, England*, ed. C. T. John, International Scholarly Book Services, Inc., 1975.
8. K. H. Valentine and E. L. Long, "Fuel Particle Inspection with an Irradiated Microsphere Gamma Analyzer," *ANS transactions*, vol. 22, TANSO 22 (1975), pp. 213-14.

9. FISSION PRODUCT RELEASE EXPERIMENTS

This chapter consists of four sections: the release of fission products during irradiation, the release of fission products from bare ThO₂ kernels during postirradiation annealing at 1400°C, the concentration profiles for ¹³⁷Cs in Biso coatings of some of the fuel particles, and a summary of fission product release experiments.

9.1 Fission Product Release During Irradiation

The differences between the calculated and measured inventories of ⁹⁵Zr, ¹⁰⁶Ru, ¹⁴⁴Ce, ¹²⁵Sb, and ¹³⁷Cs are listed, plotted, and discussed in this section. The fractional release or difference was calculated by the equation

$$FR = \frac{C - A}{C} \times 100, \quad (9.1)$$

where

FR = release or difference in % of the calculated value,

C = calculated inventory,

A = analyzed inventory.

The calculated inventories were determined differently for the fission products not expected to be released (⁹⁵Zr, ¹⁰⁶Ru, and ¹⁴⁴Ce) than for those released (¹²⁵Sb and ¹³⁷Cs). The methods of calculation are discussed below. The number of particles in each sample should be considered in the interpretation of the graphs. The raw data and the standard derivations are given in Appendix B, Table B.1.

No release of ⁹⁵Zr, ¹⁰⁶Ru, and ¹⁴⁴Ce was expected during irradiation of the Biso-coated ThO₂ particles. The differences between calculated and measured inventories of ⁹⁵Zr, ¹⁰⁶Ru, and ¹⁴⁴Ce are listed in Table 9.1. The calculated values of these fission products were based on the average neutron flux at the horizontal midplane (HMP) determined from the analyzed inventories of ⁹⁵Zr, ¹⁰⁶Ru, and ¹⁴⁴Ce and multiplied by the attenuation factors for distance from the HMP. The neutron fluxes are given in Table 6.4 in Sect. 6, and the calculations for the inventories of the fission products are described in the same section. The values in Table 9.1 are plotted vs burnup in Figs. 9.1, 9.2, and 9.3. The burnups are those determined from the fission product inventories. The differences between calculated and measured inventories show no relation to temperature, and those for ⁹⁵Zr and ¹⁰⁶Ru show a decrease with burnup. This trend with burnup and the variation in the results for different fission products may reflect biased inaccuracies in analyses or input data such as effective yields, cross sections, or attenuation factors for distances used in the calculations. Also, no significant effects of coating failure beyond the scatter of the data are noted in these results.

Release of ¹³⁷Cs was expected from the Biso-coated ThO₂ particles, particularly at the higher irradiation temperature. The results of these experiments indicate that ¹³⁷Cs and ¹²⁵Sb were released at the higher temperatures and burnups; however, at the lower burnups, the ¹³⁷Cs and ¹²⁵Sb inventories calculated using the procedure for ⁹⁵Zr, ¹⁰⁶Ru, and ¹⁴⁴Ce were higher than the measured inventories. Therefore, a correction was applied to make the initial measured values correspond with the calculated values as described below.

The analyzed concentrations of ¹²⁵Sb, ¹³⁷Cs, ¹⁰⁶Ru, and ¹⁴⁴Ce in the coated particles were used to obtain neutron fluxes by interpolation of the values in Tables B.6 through B.9 (Appendix B). Since ¹⁰⁶Ru and ¹⁴⁴Ce are not expected to be released from oxide fuel particles and are the next most prominent peaks in the gamma-ray spectra of these coated particles, the neutron fluxes of the individual samples

Table 9.1. Difference between calculated and analyzed inventories of ^{95}Zr , ^{106}Ru , and ^{144}Ce in Biso-coated ThO_2 particles from HT-12 through HT-15 irradiation experiments

Sample No	Number of particles	Irradiation temperature (°C)	Burnup ^a (% FIMA)	Difference between calculations and analyses (%) ^b		
				⁹⁵ Zr	¹⁰⁶ Ru	¹⁴⁴ Ce
Coatings survived						
HT-12-8	16	1090	0.82	24	−8	0
HT-12-13	16	1180	1.01	24	−2	5
HT-12-21	16	1370	1.38	23	−7	2
HT-12-26	15	1450	1.45	19	0	6
HT-13-8	15	1190	3.66	16	−11	0
HT-13-13	15	1270	4.52	17	−8	2
HT-13-21	18	1460	6.02	6	−6	−1
HT-13-26	19	1520	6.35	15	−4	2
HT-14-8	1	1250	7.85	9	−10	4
HT-14-13	2	1320	9.63	6	−13	1
HT-14-21	12	1500	13.7	−7	−25	−9
HT-15-13	1	1330	11.8	5	−17	1
HT-15-26	19	1550	16.4	6	−10	1
Coatings failed						
HT-12-26	1	1450	1.45	26	5	12
HT-13-8	1	1190	3.66	5	−5	1
HT-14-8	14	1250	7.85	10	−12	0
HT-14-13	6	1320	9.63	6	−12	2
HT-14-21	3	1500	13.7	−2	−23	−6
HT-15-8	13	1260	9.89	3	−14	1
HT-15-13	7	1330	11.8	7	−16	2
Coatings not tested or some failed and some survived						
HT-13-29	18 ^c	1470	6.39	6	−16	−4
HT-14-13	17 ^d	1320	9.63	6	−13	1
HT-14-21	18 ^d	1500	13.7	−3	−22	−7
HT-14-26	1 ^c	1550	14.5	−8	−18	−8
HT-15-13	16 ^c	1330	11.8	5	−15	2
HT-15-29	18 ^d	1510	15.8	−2	−24	−6

^aBurnup calculated from fission product inventories

^bDifference (%) = $(C - A)/C \times 100$, where C = calculated inventory and A = analyzed inventory. Calculations based on average neutron flux determined from ^{95}Zr , ^{106}Ru , and ^{144}Ce inventories

^cCoated particles not tested by hot chlorine leach

^dIncludes particles tested and listed above plus some not tested

Fig. 9.1. Difference between calculated and analyzed inventories of ^{95}Zr in fertile particles from capsules HT-12 through HT-15.

Fig. 9.2. Difference between calculated and analyzed inventories of ^{106}Ru in fertile particles from capsules HT-12 through HT-15.

Fig. 9.3. Difference between calculated and analyzed inventories of ^{144}Ce in fertile particles from capsules HT-12 through HT-15.

used were determined from the average of the ^{106}Ru and ^{144}Ce inventories and multiplied by the average of the ratio of neutron flux determined from the ^{137}Cs and ^{125}Sb to the average of that determined from ^{106}Ru and ^{144}Ce in the low-burnup samples. These ratios were 1.07 and 1.09 respectively. These neutron fluxes were then used to determine the ^{137}Cs and ^{125}Sb produced in the coated particles. The use of the neutron flux obtained from the average ^{144}Ce and ^{106}Ru inventories in each sample, corrected by the appropriate ratios as applicable rather than use of average neutron fluxes multiplied by attenuation factors, eliminated errors due to particle size or neutron flux variations.

The fractional releases of ^{137}Cs and ^{125}Sb are listed in Table 9.2 and are plotted vs burnup in Figs. 9.4 and 9.5. The data in Fig. 9.1 show no significant loss of cesium to a burnup of about 2% FIMA at either 1200 or 1500°C. At 1200°C no loss is apparent until a burnup of 4.5% FIMA is exceeded. The release of 20% of the cesium at 6% FIMA indicates that losses occur earlier at 1500°C and are higher with temperature and burnup, as would be expected. The effects of coating failures are difficult to assess. In most samples, all or nearly all of the coatings either survived or failed; therefore, direct comparisons are limited. Also, the time of failure cannot accurately be determined. The data show no effect of coating failure at lower burnups, but a possible higher release at the higher burnups. The data in Fig. 9.2 show an increase in ^{125}Sb release with burnup, but no definite effects of temperature or coating failure within the scatter of the data.

Table 9.2. Loss of antimony and cesium from Biso-coated ThO₂ particles in capsules HT-12 through HT-15 during irradiation

Sample No	Number of particles	Irradiation temperature (°C)	Burnup ^a (% FIMA)	Loss (%) ^b	
				¹²⁵ Sb	¹³⁷ Cs
Coatings survived					
HT-12-8	16	1090	0.82	-3.3	0.5
HT-12-13	16	1180	1.01	-2.8	0.1
HT-12-21	16	1370	1.38	-2.9	0.2
HT-12-26	15	1450	1.45	-3.0	0.6
HT-13-8	15	1190	3.66	3.6	0.0
HT-13-13	15	1270	4.52	7.4	-0.8
HT-13-21	18	1460	6.02	16.6	20.3
HT-13-26	19	1520	6.35	9.5	20.8
HT-14-8	1	1250	7.85	6.9	-5.8
HT-14-13	2	1320	9.63	22.2	18.7
HT-14-21	12	1500	13.7	23.6	42.4
HT-15-13	1	1330	11.8	15.9	15.7
HT-15-26	19	1550	16.4	34.2	29.0
Coatings failed					
HT-12-26	1	1450	1.45	-8.2	-3.1
HT-13-8	1	1190	3.66	2.0	-1.6
HT-14-8	14	1250	7.85	12.5	1.2
HT-14-13	6	1320	9.63	14.8	6.9
HT-14-21	3	1500	13.7	27.9	64.9
HT-15-8	13	1260	9.89	12.6	39.4
HT-15-13	7	1330	11.8	18.1	51.2
Coatings not tested or some failed and some survived					
HT-13-29	18 ^c	1470	6.39	9.5	6.6
HT-14-13	17 ^d	1320	9.63	14.7	10.6
HT-14-21	18 ^d	1500	13.7	26.0	45.9
HT-14-26	1 ^c	1550	14.5	24.0	59.5
HT-15-13	16 ^c	1330	11.8	18.2	47.2
HT-15-29	18 ^d	1510	15.8	27.2	55.3

^aBurnup calculated from fission product inventories

^bLoss (%) = $(C - A)/C \times 100$, where C = calculated inventory and A = analyzed inventory. Calculations based on ¹²⁵Sb and ¹³⁷Cs inventories in low-temperature low-burnup samples (see text)

^cIncludes coated particles tested and listed above

^dCoated particles not tested by hot chlorine leaching plus some not tested

9.2 Cesium, Antimony, and Europium Release from Bare ThO₂ Kernels During Postirradiation Anneals

The experiments described in this section were conducted to determine the release rate of cesium from the kernels and to obtain approximate diffusion coefficients. Kernels were separated from the coated particles and were annealed at 1400°C. The annealing system and procedure have been described previously.^{1,2} Eight tungsten tubes were inserted in holes in a graphite crucible and heated by induction. Each tube contained one kernel. The tubes were removed at various intervals, the kernels were removed, and the tubes and kernels were analyzed for ¹³⁷Cs products, using a sodium iodide gamma-ray detector.

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Fig. 9.4. Release of ^{137}Cs from Bisected ThO_2 particles during irradiation in capsules HT-12 through HT-15.

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Fig. 9.5. Release of ^{125}Sb from Bisected ThO_2 particles during irradiation in capsules HT-12 through HT-15.

The kernels were then replaced in the tubes, and the anneal was continued. Peaks for ^{125}Sb and ^{134}Cs were found and subtracted to obtain accurate ^{137}Cs analyses, but the ^{125}Sb peak was not distinct enough for accurate ^{125}Sb analyses. However, after the annealing series ended, the kernels and tubes were analyzed on another system with a germanium detector in order to obtain the fraction of ^{125}Sb and ^{154}Eu released and to verify the ^{137}Cs release values. After annealing the kernels for 684 hr at 1400°C , the cesium release from kernels taken from HT-12-8, HT-12-13, HT-13-8, and HT-13-13 was less than 1% of the total in the kernels at the beginning of the anneal. The accumulative cesium release fractions at various times are given in Table 9.3. The slope and intercept for a least-squares fit of the data vs time, the kernel diameters, and the ^{137}Cs in the separated coatings are also presented.

A typical plot of cesium release vs annealing time is shown in Fig. 9.6. The line on the graph represents a least-squares fit of the data. From the slope of the line and the average radii of the kernel, the diffusion coefficient (D) was obtained by the equation

$$D \cong \frac{F^2 a^2 \pi}{36 t}, \quad (9.2)$$

where

F = fraction of cesium released in time t ,

a = radius of the kernel.

Fig. 9.6. Cesium release from bare ThO_2 kernel during postirradiation anneal at 1400°C .

Table 9.3. Cesium release from bare kernels of ThO₂ during postirradiation anneals at 1400°C

	Time (hr)	Capsule (% collected)							
		HT-12-8-1	HT-12-8-2	HT-12-13-1	HT-12-13-2	HT-13-8-1	HT-13-8-2	HT-13-13-1	HT-13-13-2
	6	0.17	0.019	0.023	0.067	0.10	0.02	0.06	0.09
	12	0.18	0.020	0.024	0.078	0.10	0.02	0.07	0.10
	28	0.19	0.021	0.029	0.080	0.09	0.02	0.05	0.09
	72	0.20	0.028	0.047	0.10	0.18	0.10	0.16	0.15
	136	0.21	0.018	0.054	0.12	0.34	0.26	0.25	0.18
	208	0.24	0.026	0.069	0.12	0.42	0.38	0.35	0.28
	293	0.22	0.034	0.083	0.14	0.35	0.32	0.50	0.35
	452	0.26	0.031	0.082	0.15	0.61	0.56	0.61	0.45
	684	0.27	0.047	0.130	0.17	0.69	0.66	0.92	0.67
Intercept ^a (%)	f_0	0.165	0.015	0.0090	0.0615	-0.0057	-0.0935	-0.106	-0.0245
Slope ^a (%/√hr)	m	4.138E-3	9.816E-4	4.174E-3	4.276E-3	2.657E-2	2.885E-2	3.555E-2	2.339E-2
Kernel diam (cm)	k	381E-4	394.5E-4	501.0E-4	494.0E-4	403.0E-4	396.2E-4	500E-4	501.5E-4
Fraction in coatings ^b (%)	f_a	15	4	2	5	6	3	3	8

^aSlope and intercept from least-squares fit of data to equation $f = f_0 + mt^{1/2}$, where f = fraction released.

^b f_a (%) = $(P - K)/P \times 100$; here P is the total cesium in the particle before grinding, and K is the amount in the kernel.

This equation, adapted from Booth and Rymer,³ is good for an approximation up to a release of 20%. The use of the kernel radius instead of the unknown radius of the grains in the kernel will introduce some error, and the calculated values for D will be larger than the true values. Diffusion coefficients for cesium in the eight kernels are listed, together with the total cesium, antimony, and europium release at 684 hr in Table 9.4.

Another annealing experiment on bare kernels irradiated to higher burnups from capsules HT-14 and HT-15 was attempted, however, most of the kernels disintegrated on heatup. The anneal will continue on four remaining kernels.

Table 9.4. Cesium diffusion coefficients and final fractions for cesium, antimony, and europium release in bare kernels of capsules HT 12 through HT-15 during postirradiation anneals at 1400°C

Coated-particle No	Fraction released in 684 hr (%)			Cesium diffusion coefficient (cm ² /sec)
	¹³⁷ Cs	¹²⁵ Sb	¹⁵⁴ Eu	
HT-12-8-1	0.27	1.20	0.0	1.5×10^{-17}
HT-12-8-2	0.047	0.76	0.0	9.1×10^{-19}
HT 12-13-1	0.130	5.21	1.4	2.6×10^{-17}
HT 12-13-2	0.17	0.49	0.0	2.7×10^{-17}
HT-13-8-1	0.69	17.35	11.4	7.0×10^{-16}
HT 13-8-2	0.66	16.35	9.4	7.9×10^{-16}
HT 13-13-1	0.92	19.26	15.6	1.9×10^{-15}
HT-13-13-2	0.67	20.89	20.5	8.3×10^{-16}

9.3 Cesium Concentration Profiles in Pyrocarbon Coatings

Cesium concentration profiles in coatings of particles from capsules HT-12 and HT-13 have been obtained by grinding. The apparatus used is shown in Fig. 9.7. Three separate motions are provided to ensure even grinding and to maintain sphericity. The coatings are removed in steps. After each cut, the abrasive disk is removed for analysis and replaced with new abrasive paper. A typical profile of cesium concentration in the coating of a particle from HT-13-8 is shown in Fig. 9.8. For comparison, a typical cesium concentration profile for a coated UO₂ particle irradiated to a higher burnup and which demonstrated constant-potential cesium transport is shown in Fig. 9.9. The lower concentrations shown in Fig. 9.8 reflect the low cesium release from this particle. The shape of the profile with a higher concentration at the outer boundary would indicate a variation in cesium solubility in the coating with radial position. This variation in coating characteristics with radial position is also seen in the grinding rate as a function of radial position plotted in Fig. 9.10. In this graph, the volume removed per unit time represents the grinding rate while the grinder was maintained at constant conditions of applied voltage and lubrication. However, the grinder was not designed to maintain constant grinding rates; also, there is a possible variation of grinding rate with particle diameter inherent in the grinding process. Therefore, the curves can be used only for qualitative comparisons. The graph shows that the coatings of the batch OR-1849 particles were softer at the outer boundary. This effect was not as pronounced in the OR-1840 particles. The rise in grinding rate in the outer coating at the buffer interface might be due partially to errors in determining this boundary. The graph shows a decrease in grinding rate in the buffer as the kernel is approached in the OR-1849 particles. The buffer broke away in the smaller OR-1840 particles, preventing us from obtaining profile information in the buffers of these coated particles.

Fig. 9.7. Coated particle grinder.

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Fig. 9.8. Cesium concentration in coating of particle from HT-13-8.

Fig. 9.9. Cesium concentration profile in pyrocarbon coating of UO_2 particle irradiated to 11% FIMA and annealed 30 hr at 1400°C .

Fig. 9.10. Coated particle grinding rates.

9.4 Summary and Discussion of Fission Product Release Experiments on Biso-Coated ThO₂ Particles from Batches OR-1838, OR-1840, and OR-1849

Some of the conclusions to be drawn from the fission product analyses after irradiation may be in doubt because of several inconsistencies. The ratios of analyzed-to-measured inventories of the various fission products do not agree, and these ratios increase (or the apparent release decreases) with burnup for ⁹⁵Zr and ¹⁰⁶Ce, which is not as expected. These problems are probably caused by the use of incorrect input data in the calculated values. Further research is necessary to obtain correct yields and reaction rates for the HFIR-HT experiments. The decrease and negative values in the apparent release of ⁹⁵Zr, ¹⁰⁶Ru, and ¹⁴⁴Ce as burnup increases indicate the probable retention of these fission products to burnups of 16% and temperatures to 1550° C in the coated particles examined. The burnups used here are the more conservative values obtained from the fission product inventories.

The calculations for the release of ¹²⁵Sb and ¹³⁷Cs were based on the neutron fluxes determined from the ¹⁰⁶Ru and ¹⁴⁴Ce inventories in individual samples and were normalized to make the values of release from low-burnup, low-temperature samples equal to zero. This procedure avoided some of the above problems, since the ratio of the long-lived fission products is not greatly changed with neutron flux or burnup, and the effect of variations in particle size is canceled.

The release of ¹²⁵Sb increases almost linearly with burnup from zero at about 2% FIMA to a value of about 35% release at 16% FIMA. No effect of temperature or coating failures is apparent. The release of ¹³⁷Cs, on the other hand, seems to begin at about 2% FIMA for the high-temperature samples and between 5 and 8% FIMA for the low-temperature samples. Coating failures have no effect at low burnups but seem to cause a higher release at higher burnups. The cesium release increases with burnup to between 30 to 60% at 16% FIMA in the high-temperature samples.

The lack of an effect of temperature on the release of ¹²⁵Sb is puzzling. The absence of an effect of coating failures can be explained if the kernel provides the control of the release. On the other hand, if the coating fails on an oxide fuel particle, the loss of CO would allow a reaction between the fuel and the pyrocarbon at high temperatures.⁴ This should cause increased fission product release. The increase in release with burnup for both ¹²⁵Sb and ¹³⁷Cs is probably due to changes in the kernel. Previous postirradiation experiments¹ with Biso-coated UO₂ particles irradiated to 11 and 22% FIMA, respectively, showed little effect of burnup on the diffusion of cesium in the coatings and a trapped fraction of up to about 33% at 1250° C in the lower-burnup samples. Other experiments in the same series indicated a trapped fraction of about 95% of the cesium in Biso-coated ThO₂ particles irradiated to 3.5% FIMA and annealed at 1400° C. It is postulated that a certain fraction of cesium is available in the buffer coating and in accessible regions of the kernel, whereas the rest must diffuse at a much slower rate from more inaccessible sites within the kernel. It is reasonable to expect that the trapped fraction will change with burnup because of increased porosity, changes in structure, and replacement of fuel with certain fission products as burnup increases. The increased cesium release in particles with defective coatings indicates some control of the release by nondefective coatings.

The low cesium release during irradiation at about 1250° C to burnups up to about 5% and an irradiation time of about 2000 hr in these experiments agrees with the postirradiation experiment cited above, where 95% of the cesium remained trapped at 1400° C. In these cases, most of any cesium released is due to fission fragment recoils. The annealing experiments on Biso-coated UO₂ particles showed that the breakthrough time for cesium to penetrate LTI pyrocarbon coatings of similar thickness was about 300 hr.

The release of ¹³⁷Cs and ¹²⁵Sb from bare kernels during anneals at 1400° C also showed an effect of burnup. No rapid release of an "available" fraction of cesium was demonstrated here, contrary to that

observed in previous experiments¹ on bare UO_2 -coated particles irradiated to higher burnups. The available fraction here consists of the cesium in the coatings plus whatever was released during irradiation. Although the absolute release during irradiation could not be determined exactly, the near-zero relative release over the 2000-hr period to a burnup of 5% is supported by the postirradiation experiment at 1400°C in the bare kernels, where $<1\%$ of the cesium was released in 684 hr. The fraction of cesium in the coatings removed was approximately 5%. The higher value in HT-12-8-1 was caused by accidentally grinding slightly into the surface of the kernel during removal of the coating. In many cases the buffer layer was removed by pressure applied by hand after the outer coatings were removed. In others, the buffer layer broke away during grinding, resulting in some abrasion to the kernel. These differences in the kernel surfaces may account for some of the different release fractions observed during the anneals of identical particles.

The approximate diffusion coefficients calculated here for cesium diffusion in the kernels describe the rate of release of the "trapped fraction." The diffusion coefficients in the kernel increase with burnup. At higher burnups and temperatures, the entire cesium inventory becomes available to the coating; thus the slower rate of transport through the coating becomes dominant. At higher concentrations the cesium release may be limited by a constant potential at the inner boundary of the outer coating.¹

The low cesium concentration profiles in the outer coating also confirm that the cesium release in the lower-burnup, lower-temperature samples of these experiments is kernel-controlled.

To date, there have been no reports of significant amounts of ^{125}Sb in the coolant circuits of test reactors. This may be due to the low yield for ^{125}Sb , 0.025% from ^{235}U , and 0.11% from ^{233}U . The larger yield from ^{233}U may account for the fact that the ^{125}Sb is noticeable in the fission product release experiments on thorium fuel, whereas it was rarely found in experiments on enriched UO_2 . The fission products ^{137}Cs , ^{90}Sr , and ^{110}Ag are generally regarded as the major hazards. Silver has not been detected in the coated particles from these experiments.

References

1. M. T. Morgan, H. J. de Nordwall, and R. L. Towns, *Release of Fission Products from Pyrocarbon-Coated HTGR Fuel Particles During Postirradiation Anneals*, ORNL/TM-4539 (December 1974).
2. M. T. Morgan and R. L. Towns, *Techniques and Apparatus for Inspection, Handling, and Annealing Highly Radioactive Fuel Microspheres*, ORNL/TM-2495 (March 1969).
3. A. H. Booth and G. T. Rymer, *Determination of the Diffusion Constant of Fission Xenon in UO_2 Crystals and Sintered Compacts*, Report No. CRDC-721 (September 1957).
4. J. R. Piazza and M. J. Sinnott, "High-Temperature Phase Equilibria in the System Carbon-Oxygen-Uranium," *J. Chem. Eng. Data* 7(4), 451-57 (October 1962).

10. CHARACTERIZATION OF PYROCARBON COATINGS

Characterization measurements were made on the pyrocarbon (PyC) LTI coating of archives of Biso-coated fuel particles. Selected batches, OR-1749, OR-1838, and OR-1849, were examined by using optical anisotropy (OPTAF), plasma oxidation, and transmission electron microscopy (TEM) techniques. Each of these batches showed excellent survival rates, per visual inspection, in capsules HT-12 through HT-15, with the exception of batch OR-1749 in capsule HT-14 (Table 4.1). However, some of these coated particles developed permeability during irradiation. Investigations were conducted at ORNL and at KFA-IRW,¹ Jülich, Republic of Germany.

10.1 Optical Anisotropy

Special metallographic samples of particles from the HT-12 through HT-15 series were prepared for OPTAF measurements. After OPTAF measurements were completed at ORNL, the particles were shipped to Jülich for additional examination. Seventeen particles from each of the batches were arranged in a 4×4 array in a metallographic mount with the seventeenth particle serving as an index mark. This arrangement provided for identification of five specific particles measured in each sample set. The optical measurements included maximum and minimum relative reflected intensities used for calculation of OPTAF values and also absolute reflectivities.

The twofold symmetry OPTAF values obtained by the two laboratories using air objectives are shown in Table 10.1. The agreement between the OPTAF values obtained for a specific ORNL coating by the two laboratories is well within the ORNL estimated variance of ± 0.015 OPTAF unit for values in the range of 1.03 to 1.00. These results indicate that for a specific PyC specimen, the ORNL and KFA-IRW values are essentially identical.

Table 10.1. OPTAF^a measurements on ORNL PyC coatings made at ORNL and KFA-IRW, Jülich

Particle designation	OPTAF	
	ORNL ^b	(KFA-IRW) ^{b,c}
OR-1749	1.03	1.027
OR-1838	1.02	
OR-1849	1.02	1.033

^aBased on maximum and minimum reflectivity using polarizer only, wavelength = 5470 Å.

^bMidradius value of PyC coating.

^cMeasurements made on Leitz MPV-II system.

10.2 Plasma Oxidation

The technique for selective etching of PyC fuel particle coatings by an rf-excited oxygen plasma was developed such that etch features during etching could be resolved optically at magnifications in excess of 500 $\times$. Standard epoxy metallographic mounts containing the fuel particles of interest were polished to expose the midplane of the particle coatings. The polished coatings were first used for OPTAF measurements and then were etched in the oxygen plasma. The etcher contains two chambers, and the rf power (at 13.5 MHz) in each chamber was maintained at 20 W, with the oxygen pressure at 0.75 torr. A

detailed description of this technique is described in ref. 2. The technique employed by KFA-IRW is similar except that their etcher contains more than two chambers.

Observations of polished surfaces of various PyC coatings in polarized light at about 60 $\times$ indicate that they consist of two optically discernible varieties of carbon. One is optically anisotropic and is visible at 500 $\times$ or above as very small regions of optical activity. These small regions exhibit four maxima of reflected intensity during a 360 $^\circ$ rotation of the polarization vector in the light beam relative to some reference direction on the PyC midplane surface. The deposition and apparent concentration of these optically active regions vary greatly in PyC coatings produced in different sized coaters and under various coating conditions. The other variety of carbon present in the coatings is optically inactive by microscopic observation under crossed polars. In some cases the regions containing this carbon exist over distances of several micrometers.

Oxidation occurs most rapidly in coating regions where the optically inactive carbon is concentrated in the LTI PyC. These regions are designated ROC (readily oxidizable carbon). The regions where the optical domains are concentrated oxidize relatively slowly, and these regions are designated POC (poorly oxidizable carbon). This differential in oxidation rates produces the surface relief in an originally polished PyC surface that can be observed using dark-field illumination. The relief structure produced by plasma oxidation thus provides an indication of the locations of regions having high concentrations of the optically active carbon in the coating. Workers at KFA have reported that the geometric disposition and concentration of the less oxidizable carbon have an important bearing on the fast-neutron damage resistance of a PyC LTI coating. Coating structures in which this optically active carbon is present in continuous spherical shells in the coating have been reported by KFA to be much more sensitive to failure because of fast-neutron damage than structures in which the two varieties of carbon, deduced from etching results, are distributed in such a way that the poorly oxidizing carbon does not form continuous shells. This concept has been confirmed through plasma oxidation and irradiation data for coating types irradiated in HT-17 through HT-19.³

Coating OR-1849, which contained a 75- μ m-thick LTI, was examined by plasma oxidation at ORNL and at KFA. Figure 10.1 [(a) and (b)] shows dark-field photomicrographs of KFA's results at 500 $\times$ and 1000 $\times$ respectively. Figure 10.2 is a dark field of ORNL's results at 500 $\times$. In each case it was found that coating OR-1849 contained a large quantity of ROC and the distribution was homogeneous, with the exception of the layer adjacent to the buffer layer. This etch structure agrees well with the survival criteria discussed previously.

Coating OR-1749, which had a nominal LTI design thickness of about 36 μ m, was also examined by ORNL and KFA. Figure 10.3 [parts (a) and (b)] shows dark-field photomicrographs of KFA's results on this coating at 500 $\times$ and 1000 $\times$ respectively. Figure 10.4 is a similar photomicrograph of ORNL's results at 500 $\times$. As can be seen, this coating exhibited wide ROC bands running nearly continuously through the coating. The regions between the bands are made up almost entirely of POC. This coating typically exhibited a structure having two or three bands of POC alternating with bands of ROC along the coating radius. In contrast to the survival criteria presented earlier, this coating type showed good irradiation performance (per visual inspection) in spite of the banded structure.

Coating OR-1838, which had a nominal LTI thickness of 64 μ m, was examined by ORNL only. Figure 10.5 is a photomicrograph of ORNL's results at 500 $\times$. This coating exhibited an etch structure that consisted of two or three zones of finely spaced bands of POC with alternate bands of ROC. Some particle coatings contained two of the clustered bands, whereas others exhibited three during the etching procedure. This coating also showed good survival (per visual inspection) in capsules HT-12 through HT-14.

Fig. 10.1. Ceramographic section of particle charge OR-1849 HT plasma-oxidized. (a) 500:1; (b) 1000:1.

Fig. 10.2. Dark-field photomicrograph of ORNL's plasma oxidation results for coating OR-1849.

10.3 Transmission Electron Microscopy

ORNL coating OR-1849 was examined by TEM.⁴ Samples were prepared by hot pressing a mixture of LTI fragments and aluminum powder. A slice of this mount was ground to about 1 to 2 mils in thickness, then thinned by argon ion-milling until sufficiently thin for electron transmission. The specimen was observed in both the bright- and dark-field modes. For dark-field imaging the diffraction aperture was located on the (002) reflection of the pyrocarbon structure; coherently diffracting regions within the growth features appeared in the image.

A close examination of TEM results on various ORNL coatings (including OR-1849) revealed that the LTI coatings contain two size ranges of structural features. Each range consists of spherical growth features which contain zones about their periphery in which pyrocarbon crystallites are present on a dimensional scale of about 1000 Å. These pyrocarbon crystallites are arranged with their *c* axes approximately parallel with the radius of the growth feature. The core contains clusters of spherical objects with a diameter of about 100 Å, which are thought to be nuclei for the formation of the growth feature. The size of the growth features depends on the number of layers of crystallites around the periphery. In the large size range, the growth feature contains many layers of the peripheral pyrocarbon crystallites, whereas in the smaller size range, the growth features contain fewer peripheral crystallites and the primary constituent is the nucleus cluster. Regions where there is a high concentration of the smaller growth features are thought to be the ROC regions as determined by plasma oxidation. The most easily oxidizable carbon is thought to be the nuclei clusters. Those regions where there is a high concentration of the large-diameter growth features are the POC regions as determined by plasma oxidation.

Fig. 10.3. Ceramographic section of particle charge OR-1749 HT plasma-oxidized. (a) 500:1; (b) 1000:1.

Fig. 10.4. Dark-field photomicrograph of ORNL's plasma oxidation results for coating OR-1749.

Fig. 10.5. Dark-field photomicrograph of ORNL's plasma oxidation results for coating OR-1838.

Figure 10.6 is a transmission electron photomicrograph of coating OR-1849 in bright field, showing spherical or partially spherical growth features. Some growth feature boundaries are indicated at positions *A*, *B*, and *C*. Typical diameters for these growth features are on the order of $0.5\ \mu\text{m}$. Figure 10.7 is a similar photomicrograph but in dark field of the same area. The comparable feature boundaries are marked. The bright areas indicate regions containing coherently diffracting crystallites that correspond to the particular diffracted intensity used to form the image.

Fig. 10.6. Transmission electron photomicrograph of coating OR-1849 in bright field, showing spherical or partially spherical growth features at positions *A*, *B*, and *C*.

Fig. 10.7. Transmission electron photomicrograph of coating OR-1849 in dark field, showing spherical or partially spherical growth features at positions *A*, *B*, and *C*, corresponding to Fig. 10.6.

10.4 Discussion

The results from the characterization of the pyrocarbon LTI coatings on ORNL designs OR-1838, OR-1849, and OR-1749 have contributed to the overall effort of understanding the nature of the LTI pyrocarbon coating. The efforts at KFA-IRW, Jülich, and at ORNL have yielded results that are quite consistent. The OPTAF values for the three coatings listed above (as determined by the two laboratories) are essentially identical. The OPTAF values measured were in the range of 1.02 to 1.03 for each coating design.

The plasma oxidation results for coating OR-1849, which contained a 75- μ -thick LTI, indicated that it contained a large quantity of ROC material. The distribution of this material was found to be homogenous, with the exception of the layer adjacent to the buffer layer. From the coatings investigated for this experiment, it agreed best with the survival criteria discussed earlier. Also, this coating showed good irradiation survivability as determined by visual PIE.

Plasma oxidation results for coating OR-1749, which had a nominal LTI design thickness of about 36 μ , indicated that this coating exhibited wide ROC bands running nearly continuously through the coating. The regions between these bands were made up almost entirely of POC material. This coating typically exhibited a relief structure of two or three bands of POC alternating with bands of ROC. In contrast to the survival criteria, the irradiation performance (per visual inspection) was much better than would have been anticipated.

Plasma oxidation of coating OR-1838, which had a nominal 64- μ -thick LTI, exhibited an etch structure of two or three zones of finely spaced bands of POC with alternate bands of ROC. This coating had good irradiation performance as determined by visual PIE.

The TEM results revealed that the pyrolytic LTI coatings (from various studies including OR-1849) are composed of two size ranges of growth features. The core of these spherical growth features contains clusters of spherical objects which are thought to be nuclei for the formation of the growth feature. Regions that contain a large concentration of the large growth features are thought to be the POC regions as determined by plasma oxidation. Regions with a high concentration of the smaller growth features are thought to be the ROC regions, with the nuclei clusters being the most easily oxidizable carbon.

References

1. Personal communication from H. Luhleich, KFA-IRW, Jülich, to V. J. Tennery, ORNL, May 1975.
2. J. P. Mathers, V. J. Tennery, and E. S. Bomar, *Equipment Variables and Deposition Conditions Affecting the Plasma Oxidation of Pyrocarbon Coatings on HTGR Fuel Particles*, ORNL/TM-5308 (June 1976).
3. R. L. Beatty et al., *Irradiation Performance of HTGR Fertile Fuel in HFIR Target Capsules HT-17, HT-18, and HT-19* (in preparation).
4. C. S. Yust, V. J. Tennery, H. P. Krautwasser, and R. L. Beatty, *Structural Characterization of HTGR Pyrocarbon Fuel Particle Coatings* (in preparation).

11. CONCLUSIONS

The results from irradiation of HFIR target capsules HT-12 through HT-15 and their subsequent postirradiation analyses have shown the following:

1. The LTI coatings, deposited using high LTI coating rates of approximately $20 \mu\text{m}/\text{min}$, which did not fail due to the pressure vessel failure mechanism, were batches OR-1838, OR-1840, and OR-1849. Coated particles from batches OR-1840 and OR-1849 were further examined by hot chlorine leaching and gas-pressure methods. These tests indicated that some of the coated particles developed permeability during irradiation, in particular, particles irradiated at a temperature $\cong 1250^\circ\text{C}$ and with burnups of $\geq 8\%$ FIMA. In contrast, particles from the same batches showed no permeability at an irradiation temperature $\cong 1550^\circ\text{C}$ and at burnups $\cong 16\%$ FIMA. The nature of the permeability could not be determined by scanning electron micrographs. If further evidence shows that irradiation-induced permeability is a serious problem, then the design of coatings should be directed toward those resistant to both pressure vessel failure and irradiation-induced permeability.

2. The method of failure determination by visual inspection is not sufficient to determine the integrity of coated particles. To detect permeability in irradiated coatings, visual inspection must be followed by a more thorough inspection of the apparent intact coated particle. Both hot chlorine leach and fission gas measurements gave nearly equivalent indication of failed or intact particles. It is recommended that future failure determinations on Biso coatings be made by the hot chlorine leaching process or by the irradiated microsphere gamma analyzer, in addition to the PIE visual inspection.

3. Particle sample holders operated between 50 and 200°C higher than original design temperatures, depending on holder location in a particular graphite magazine. The holder temperatures by themselves were not adequate in describing particle operating temperatures. Maximum particle surface temperatures exceeded sample holder temperatures by as much as 100°C after one HFIR cycle and peaked at approximately 300°C higher during the fourth cycle in the high-temperature regions and in the sixth cycle in the low-temperature regions. In general, the particle operating temperatures in the low-temperature regions were 1200 to 1300°C ; in the high-temperature regions they were 1500 to 1600°C .

4. The extremes in temperature and fast neutron fluence had a pronounced effect on the performance of the Poco graphite sample holders and magazines. The sample holders experienced severe swelling, in excess of 9.5% , and distortion in capsule HT-15. The swelling of the graphite magazines in HT-15 completely closed the gap between the magazines and the aluminum containment. To avoid possible interference between fuel performance and graphite performance, it is recommended that future loose coated-particle capsules be limited to fluences about one and one-half HTGR design (approximately six HFIR cycles).

5. The percentage of the theoretical amount of krypton + xenon released into the void space of the intact ThO_2 particles appeared to be primarily dependent on burnup and reached $\sim 90\%$ at design burnup. The present results agreed with those determined by Janvier et al.¹ for 80 to 90% dense UO_2 kernels irradiated to 2 to 8% FIMA at 1000 to 1400°C .

6. Oxygen release per fission (O/f) is a function of temperature and burnup and can be expressed by Eq. (7.1) for ThO_2 particles irradiated in the target region and stored out-of-reactor for approximately two years. Oxygen release is apparently significantly affected by the interaction of sesquioxides of yttrium and rare-earth elements with uranium to form UO_{2+x} . Calculated in-HFIR O/f values at 5% FIMA are smaller than the measured amounts because of the presence of significant concentrations of the 27-day PaO_{2+x} . Calculated in-HTGR O/f values at 5% FIMA are larger than those measured in the present experiments because the in-HTGR concentrations of UO_{2+x} are about half of those in the present HT particles.

7. The coated particles showed complete retention of fission products ^{106}Ru and ^{144}Ce to burnups of 16% FIMA and at irradiation temperatures of 1550°C. Fission products ^{137}Cs and ^{125}Sb were lost under these same conditions. No ^{110}Ag was detected in the particles examined. Cesium loss ranged from 0 to 40% in coated particles for burnups of 6 to 16% FIMA with coatings impermeable to hot chlorine leach, and up to approximately 65% in particles with defective coatings at the higher temperatures. At the lower temperatures the cesium loss was <1% at burnups of <8% FIMA.

References

1. J. C. Janvier, M. Bruet, and R. Blanchard, "Fission Gas Pressure Evolution in Irradiated Coated Particles," *Proc. Conf. on the HTGR, London, 1973*, British Nuclear Energy Society, preprint No. 34.

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APPENDIX A

Operating Temperature Histories for Loose-Coated Particles Irradiated in HT-12 through HT-15

ORNL-DWG 75-7483

HT-12&13 PARTICLE HOLDER 2 BATCH GA-4252-08
815.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7484

HT-12&13 PARTICLE HOLDER 4 BATCH OR-1850
694.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7485

HT-12&13 PARTICLE HOLDER 5 BATCH OR-1846
482.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7486

HT-12&13 PARTICLE HOLDER 7 BATCH GA-4252-00
719.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7487

HT-12&13 PARTICLE HOLDER 8 BATCH OR-1840
552.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7488

HT-12&13 PARTICLE HOLDER 10 BATCH GA-4252-06
822.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7489

HT-12&13 PARTICLE HOLDER 11 BATCH OR-1749
540.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7490

HT-12&13 PARTICLE HOLDER 13 BATCH OR-1849
816.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7491

HT-12&13 PARTICLE HOLDER 15 BATCH GA-4252-08
815.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7492

HT-12&13 PARTICLE HOLDER 17 BATCH OR-1850
694.0 MICRON PARTICLE DIAMETER

HT-12&13 PARTICLE HOLDER 18 BATCH OR-1846
482.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7494

HT-12&13 PARTICLE HOLDER 20 BATCH GA-4252-00
719.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7496

HT-12&13 PARTICLE HOLDER 21 BATCH OR-1840
552.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7497

HT-12&13 PARTICLE HOLDER 23 BATCH GA-4252-06
822.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7498

HT-12&13 PARTICLE HOLDER 24 BATCH OR-1749
540.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7499

HT-12&13 PARTICLE HOLDER 26 BATCH OR-1849
816.0 MICRON PARTICLE DIAMETER

HT-12&13 PARTICLE HOLDER 27 BATCH GA-4252-02
824.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7501

HT-12&13 PARTICLE HOLDER 29 BATCH OR-1838
594.0 MICRON PARTICLE DIAMETER

HT-12&13 PARTICLE HOLDER 30 BATCH GA-4252-03
819.0 MICRON PARTICLE DIAMETER

HT-12&13 PARTICLE HOLDER 32 BATCH OR-1826
506.0 MICRON PARTICLE DIAMETER

HT-12&13 PARTICLE HOLDER 33 BATCH GA-4252-01
761.0 MICRON PARTICLE DIAMETER

HT-12&13 PARTICLE HOLDER 35 BATCH OR-1830
480.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7506

HT-12&13 PARTICLE HOLDER 36 BATCH GA-4252-07
677.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7507

HT-12&13 PARTICLE HOLDER 38 BATCH OR-1837
452.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7508

HT-12&13 PARTICLE HOLDER 40 BATCH GA-4252-02
824.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7509

HT-12&13 PARTICLE HOLDER 42 BATCH OR-1833
594.0 MICRON PARTICLE DIAMETER

HT-12&13 PARTICLE HOLDER 43 BATCH GA-4252-03
819.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7511

HT-12&13 PARTICLE HOLDER 45 BATCH OR-1826
506.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7512

HT-12&13 PARTICLE HOLDER 46 BATCH GA-4252-01
761.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7513

HT-12&13 PARTICLE HOLDER 48 BATCH OR-1830
480.0 MICRON PARTICLE DIAMETER

HT-12&13 PARTICLE HOLDER 49 BATCH GA-4252-07
677.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7515

HT-12&13 PARTICLE HOLDER 51 BATCH OR-1837
452.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7516

HT-14&15 PARTICLE HOLDER 2 BATCH GA-4252-08
815.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7517

HT-14&15 PARTICLE HOLDER 4 BATCH OR-1850
694.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7518

HT-14&15 PARTICLE HOLDER 5 BATCH OR-1846
482.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7519

HT-14&15 PARTICLE HOLDER 7 BATCH GA-4252-00
719.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7520

HT-14&15 PARTICLE HOLDER 8 BATCH OR-1840
552.0 MICRON PARTICLE DIAMETER

HT-14&15 PARTICLE HOLDER 10 BATCH GA-4252-06
822.0 MICRON PARTICLE DIAMETER

HT-14&15 PARTICLE HOLDER 11 BATCH OR-1749
540.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7523

HT-14&15 PARTICLE HOLDER 13 BATCH OR-1849
816.0 MICRON PARTICLE DIAMETER

HT-14&15 PARTICLE HOLDER 15 BATCH GA-4252-08
815.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7525

HT-14&15 PARTICLE HOLDER 17 BATCH OR-1850
694.0 MICRON PARTICLE DIAMETER

HT-14&15 PARTICLE HOLDER 18 BATCH OR-1846
482.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7527

HT-14&15 PARTICLE HOLDER 20 BATCH GA-4252-00
719.0 MICRON PARTICLE DIAMETER

HT-14&15 PARTICLE HOLDER 21 BATCH OR-1840
552.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7529

HT-14&15 PARTICLE HOLDER 23 BATCH GA-4252-06
822.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7530

HT-14&15 PARTICLE HOLDER 24 BATCH OR-1749
 540.0 MICRON PARTICLE DIAMETER

HT-14&15 PARTICLE HOLDER 26 BATCH OR-1849
 816.0 MICRON PARTICLE DIAMETER

HT-14&15 PARTICLE HOLDER 27 BATCH GA-4252-02
824.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7533

HT-14&15 PARTICLE HOLDER 29 BATCH OR-1838
594.0 MICRON PARTICLE DIAMETER

HT-14&15 PARTICLE HOLDER 30 BATCH GA-4252-03
819.0 MICRON PARTICLE DIAMETER

HT-14&15 PARTICLE HOLDER 32 BATCH OR-1826
506.0 MICRON PARTICLE DIAMETER

HT-14&15 PARTICLE HOLDER 33 BATCH GA-4252-01
761.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7537

HT-14&15 PARTICLE HOLDER 35 BATCH OR-1830
480.0 MICRON PARTICLE DIAMETER

HT-14&15 PARTICLE HOLDER 36 BATCH GA-4252-07
677.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7539

HT-14&15 PARTICLE HOLDER 38 BATCH OR-1837
452.0 MICRON PARTICLE DIAMETER

HT-14&15 PARTICLE HOLDER 40 BATCH GA-4252-02
824.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7541

HT-14&15 PARTICLE HOLDER 42 BATCH OR-1833
594.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7542

HT-14&15 PARTICLE HOLDER 43 BATCH GA-4252-03
819.0 MICRON PARTICLE DIAMETER

ORNL DWG 75-7543

HT-14&15 PARTICLE HOLDER 45 BATCH OR-1826
506.0 MICRON PARTICLE DIAMETER

HT-14&15 PARTICLE HOLDER 46 BATCH GA-4252-01
761.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7545

HT-14&15 PARTICLE HOLDER 48 BATCH OR-1830
480.0 MICRON PARTICLE DIAMETER

HT-14&15 PARTICLE HOLDER 49 BATCH GA-4252-07
677.0 MICRON PARTICLE DIAMETER

ORNL-DWG 75-7547

HT-14&15 PARTICLE HOLDER 51 BATCH OR-1837
452.0 MICRON PARTICLE DIAMETER

APPENDIX B

Measured and Calculated Fission Product Inventories in Biso-Coated ThO₂ Particles from Irradiation Capsules HT-12 through HT-15

Measured fission product inventories at the end of irradiation from gamma-ray analyses are presented in Table B.1. Values are given in atoms of fission products per initial atom of ²³²Th, based on an average of 7.542×10^{17} atoms of initial ²³²Th in particles from batch OR-1838, holder 29, and batch OR-1840, holders 8, 21, and 29; and an average of 1.522×10^{18} atoms of thorium in particles from batch OR-1849, holders 13 and 26.

Calculated fission product inventories were obtained by an analytical solution of equations for the nuclide chain in Fig. 6.2. Input data are given in Sect. 6. Fission product inventories for the various holders are given in Tables B.2 through B.5. These are based on neutron flux values determined from ¹³⁷Cs and ¹⁴⁴Cs analyses as described in Sect. 9. Burnup values (fraction FIMA) are also presented.

The fission product inventories calculated for various neutron flux levels are given in Tables B.6 through B.9. These tables were used to determine burnups and neutron fluxes from analyzed values of fission products.

Table B.1. Average inventories of fission products in batches OR-1840 and OR-1849 Biso-coated ThO₂ particles from the HT-12 through HT-15 irradiation capsules as determined by gamma-ray analyses

Sample No. ^a	Number of particles ^b	Decay ^c time		⁹⁵ Zr ^d	¹⁰⁶ Ru	¹⁴⁴ Ce	¹²⁵ Sb	¹³⁷ Cs
HT-12-8	16	7.15E7	a/a ^c % S.D. ^e % error ^f	3.86E-4 ¹⁵ 8.5 8	2.19E-5 7.5 5	3.79E-4 3.9 2.5	1.03E-5 7.0 5	6.46E-4 2.8 0.4
HT-12-8L	15 s	8.78E7	a/a % S.D. % error	3.08E-4 ¹⁰ 26 22	2.44E-5 4.2 3.9	3.86E-4 2.7 2.2	1.06E-5 4.1 3.3	6.46E-4 1.9 0.3
HT-12-13	18	7.58E7	a/a % S.D. % error	4.88E-4 ⁴ 4.8 11	2.67E-4 6.9 5	4.56E-4 4.9 2.5	1.22E-5 6.5 5	7.76E-4 2.5 0.4
HT-12-13L	16 s	8.78E7	a/a % S.D. % error	3.95E-4 23 16	2.93E-5 3.4 3	4.75E-4 1.8 1.4	1.27E-5 4.0 2.5	7.88E-4 1.5 0.2
HT-12-21	17	7.81E7	a/a % S.D. % error	6.21E-4 9.8 11	4.15E-5 3.3 3	6.64E-4 2.7 1.6	1.73E-5 4.9 3	1.10E-3 2.7 0.2
HT-12-21L	16 s	9.03E7	a/a % S.D. % error		3.96E-5 4.1 3.1	6.44E-4 3.9 1.6	1.69E-5 3.9 2.4	1.09E-3 2.0 0.2
HT-12-26	15	7.86E7	a/a % S.D. % error	6.96E-4 11 7	4.17E-5 4.1 2.4	6.85E-4 2.0 1.2	1.77E-5 2.9 2.1	1.13E-3 2.4 0.1
HT-12-26	1 f	7.86E7	a/a	6.31E-4	3.93E-5	6.34E-4	1.75E-5	1.10E-3
HT-12-26L	15 s	9.12E7	a/a % S.D. % error	5.92E-4 ² 4.8 2.7	4.11E-5 4.8 2.7	6.75E-4 3.5 1.4	1.75E-5 3.5 2.1	1.10E-3 2.0 0.2
HT-13-8	18	6.89E7	a/a % S.D. % error	1.43E-3 8.1 7	1.44E-4 5.1 4	1.61E-3 3.5 1.9	4.04E-5 4.9 4	2.87E-3 2.3 0.3
HT-13-8L	15 s	7.88E7	a/a % S.D. % error	1.43E-3 19.1 12	1.11E-4 8.0 2	1.70E-3 3.6 1.6	4.30E-5 4.5 3	2.97 2.9 0.2
HT-13-8	1 f	6.89E7	a/a	1.63E-3	1.02E-4	1.65E-3	4.13E-5	2.88E-3
HT-13-13	15	6.96E7	a/a % S.D. % error	1.71E-3 7.8 5	1.24E-4 4.3 3	1.93E-3 3.5 1.4	4.52E-5 4.3 3.1	3.43 2.0 0.2
HT-13-13L	12 s	8.10E7	a/a % S.D. % error	1.75E-3 13.7 10	1.34 4.8 2	2.04E-3 1.6 1.2	4.80E-5 4.2 2	3.56E-3 1.4 0.2
HT-13-21	18	6.10E7	a/a % S.D. % error	2.50E-3 4.9 2.0	1.68E-4 3.6 2	2.65E-3 2.4 1.0	2.54E-5 8.4 2.8	3.58E-3 8.6 0.2
HT-13-26	19	7.08E7	a/a % S.D. % error	2.43E-3 7.3 4.6	1.79E-4 3.9 2.3	2.73E-3 2.0 1.1	5.9E-5 3.7 2.6	3.62E-3 12.1 0.2
HT-13-26L	16 s	8.89E7	a/a % S.D. % errors	2.17E-3 ² 10 10	1.71E-4 8.4 2.5	2.77E-3 5.1 1.3	5.75E-5 7.3 2.4	3.76E-3 12.2 0.12
HT-13-29	18	6.35E7	a/a % S.D. % error	2.62E-3 7.0 4	1.90E-4 7.6 4	2.85E-3 5.1 2	6.14E-5 7.5 5.7	4.59E-3 3.3 0.4

Table B.1 (continued)

Sample No. ^a	Number of particles ^b	Decay time ^c		⁹⁵ Zr ^d	¹⁰⁶ Ru	¹⁴⁴ Ce	¹²⁵ Sb	¹³⁷ Cs
HT-14-8	14	6.44E7	a/a	2.73E-3	2.26E-4	3.35E-3	7.53E-5	6.04E-3
			% S.D.	5.4	5.2	3.1	6.5	3.4
			% error	3.8	3.0	1.4	4	0.2
HT-14-8	1 s	6.44E7	a/a	2.77E-3	2.21E-4	3.21E-3	7.83E-5	6.29E-3
HT-14-13	17	6.57E7	a/a	3.40E-3	2.77E-4	3.99E-3	8.48E-5	6.48E-3
			% S.D.	3.5	3.8	2.4	5.5	7.5
			% error	3.3	2.6	1.4	3.8	0.3
HT-14-13	6 f	6.57E7	a/a	3.40E-3	2.73E-4	3.95E-4	8.44E-5	6.72E-3
			% S.D.	3.6	5	3.0	2.6	5.5
HT-14-13	2 s	6.57E7	a/a	3.40E-3	2.76E-4	3.99E-3	7.77E-5	5.93E-3
HT-14-21	18	5.52E7	a/a	4.62E-3	3.82E-4	5.38E-3	9.35E-5	5.27E-3
			% S.D.	3.2	5.2	3.2	10.1	20.4
			% error	1.5	2.4	1.3	4.5	0.4
HT-14-21	12 s	5.52E7	a/a	4.60E-3	3.82E-4	5.41E-3	9.25E-5	5.65E-3
			% S.D.	3.5	5.7	3.4	11.3	3.5
HT-14-21	3 f	5.52E7	a/a	4.57E-3	3.86E-4	5.34E-3	9.12E-5	3.42E-3
HT-14-21L	12	7.13E7	a/a	4.98E-3	4.01E-4	5.61E-3	1.04E-4	5.82E-3
			% S.D.	3.0	3.5	2.4	3.0	4.6
			% error	3	1.1	0.8	2	0.2
HT-14-26	1	5.32E7	a/a	5.11E-3	3.95E-4	5.80E-3	9.99E-5	4.15E-3
			% error	1.1	2	1.0	3.3	0.3
HT-15-8	13	6.42E7	a/a	3.33E-3	2.84E-4	4.06E-3	9.25E-5	4.65E-3
			% S.D.	3.6	4.9	2.9	4.3	13.3
			% error	4	3	1.7	4	0.4
HT-15-13	16	6.46E7	a/a	3.86E-3	3.46E-4	4.76E-3	9.94E-5	4.78E-3
			% S.D.	6.7	2.3	1.9	3.4	24.7
			% error	3	2.0	1.1	3	0.3
HT-15-13	7 f	6.46E7	a/a	3.78E-3	3.48E-4	4.75E-3	9.97E-5	4.43E-3
			% S.D.	3.8	2.5	2.4	3.5	21.2
HT-15-13	1 s	6.46E7	a/a	3.87E-3	3.52E-4	4.84E-3	1.04E-4	7.76E-3
HT-15-26	19	5.25E7	a/a	49.81E-3	4.44E-4	6.35E-3	9.78E-5	8.26E-3
			% S.D.	2.9	4.6	2.9	10.4	8.2
			% error	1.1	2.2	1	4.6	0.2
HT-15-29	19	5.57E7	a/a	5.29E-3	4.93E-3	6.64E-4	1.14E-4	5.57E-3
			% S.D.	5.5	5.8	5.0	6.4	3.5
			% error	1.3	2.1	1.1	4	0.4

^aIrradiation numbers followed by L are the same or part of the same particles of samples with the same number without L, except that L denotes those samples that have been hot chlorine leached.

^bNumbers not followed by letters are of particles not leach tested. Those followed by "s" survived leaching; those followed by "f" failed leaching.

^cThe values given following a/a are in atoms of fission product at the end of irradiation per initial atom of ²³²Th. The initial atoms of ²³²Th per particle used in the calculations were averages; 7.542E17 atoms in OR-1840 particles in holders -8, -21, and -29; and 1.522E18 atoms in OR-1849 particles in holders -13 and -26. The decay time to the time of analysis is given for comparison with the standard deviations and errors.

^dThe ⁹⁵Zr values were corrected for the ¹⁵⁴Eu contribution in the gamma-ray peaks. Since ⁹⁵Zr decayed more rapidly, many gamma-ray spectra showed no ⁹⁵Zr; therefore, in some samples the number of ⁹⁵Zr values was less than the number of particles. For these samples the number of ⁹⁵Zr values is given as a superscript.

^eThe % S.D. is the standard deviation of the fission product concentrations in the sample.

^fThe % error is the average standard deviation determined by counting statistics for the individual particles.

Table B.2. Calculated fission product in Biso-coated thoria particles from irradiation capsule HT-12
(atoms per initial atom of thorium)

HOLDER	FLUX	232TH	233PA	234PA	233U
8	3.065E+15	9.567E-01	2.226E-02	3.508E-05	7.269E-03
13	3.576E+15	9.496E-01	2.525E-02	4.502E-05	7.473E-03
21	4.366E+15	9.388E-01	2.953E-02	6.138E-05	7.585E-03
29	4.505E+15	9.370E-01	3.025E-02	6.436E-05	7.586E-03
26	4.598E+15	9.357E-01	3.072E-02	6.636E-05	7.584E-03
HOLDER	FLUX	234U	235U	236U	90SR
8	3.065E+15	4.597E-03	5.008E-04	6.082E-05	5.783E-04
13	3.576E+15	5.840E-03	6.934E-04	1.004E-04	7.344E-04
21	4.366E+15	7.848E-03	1.030E-03	1.877E-04	9.934E-04
29	4.505E+15	8.208E-03	1.093E-03	2.066E-04	1.041E-03
26	4.598E+15	8.449E-03	1.136E-03	2.198E-04	1.073E-03
HOLDER	FLUX	95ZR	106RU	137CS	144CE
8	3.065E+15	4.704E-04	2.215E-05	5.814E-04	3.954E-04
13	3.576E+15	5.983E-04	2.846E-05	7.394E-04	5.040E-04
21	4.366E+15	8.113E-04	3.922E-05	1.002E-03	6.861E-04
29	4.505E+15	8.506E-04	4.123E-05	1.051E-03	7.199E-04
26	4.598E+15	8.771E-04	4.260E-05	1.083E-03	7.427E-04
HOLDER	FLUX	125SB	FIMA		
8	3.065E+15	8.846E-06	8.616E-03		
13	3.576E+15	1.113E-05	1.097E-02		
21	4.366E+15	1.481E-05	1.491E-02		
29	4.505E+15	1.547E-05	1.564E-02		
26	4.598E+15	1.592E-05	1.613E-02		

Table B.3. Calculated fission product in Biso-coated thoria particles from irradiation capsule HT-13
(atoms per initial atom of thorium)

HOLDER	FLUX	232TH	233PA	234PA	233U
8	3.065E+15	9.065E-01	2.658E-02	3.540E-05	1.251E-02
13	3.576E+15	8.918E-01	2.951E-02	4.491E-05	1.226E-02
21	4.366E+15	8.695E-01	3.341E-02	6.016E-05	1.179E-02
29	4.505E+15	8.656E-01	3.403E-02	6.289E-05	1.170E-02
26	4.598E+15	8.630E-01	3.443E-02	6.470E-05	1.163E-02
HOLDER	FLUX	234U	235U	236U	90SR
8	3.065E+15	1.280E-02	1.995E-03	6.308E-04	2.581E-03
13	3.576E+15	1.532E-02	2.501E-03	9.541E-04	3.138E-03
21	4.366E+15	1.890E-02	3.239E-03	1.580E-03	4.020E-03
29	4.505E+15	1.948E-02	3.362E-03	1.705E-03	4.178E-03
26	4.598E+15	1.986E-02	3.443E-03	1.790E-03	4.283E-03
HOLDER	FLUX	95ZR	106RU	137CS	144CF
8	3.065E+15	1.756E-03	9.933E-05	2.612E-03	1.700E-03
13	3.576E+15	2.137E-03	1.229E-04	3.184E-03	2.082E-03
21	4.366E+15	2.743E-03	1.618E-04	4.094E-03	2.695E-03
29	4.505E+15	2.853E-03	1.689E-04	4.258E-03	2.806E-03
26	4.598E+15	2.926E-03	1.737E-04	4.367E-03	2.880E-03
HOLDER	FLUX	125SB	FIMA		
8	3.065E+15	3.817E-05	3.893E-02		
13	3.576E+15	4.560E-05	4.757E-02		
21	4.366E+15	5.680E-05	6.139E-02		
29	4.505E+15	5.874E-05	6.389E-02		
26	4.598E+15	6.003E-05	6.556E-02		

Table B.4. Calculated fission product in Biso-coated thorium particles from irradiation capsule HT-14
(atoms per initial atom of thorium)

HOLDER	FLUX	232TH	233PA	234PA	233U
8	3.065E+15	8.545E-01	2.786E-02	4.410E-05	1.150E-02
13	3.576E+15	8.324E-01	3.047E-02	5.456E-05	1.081E-02
21	4.366E+15	7.993E-01	3.376E-02	7.045E-05	9.815E-03
29	4.505E+15	7.936E-01	3.426E-02	7.318E-05	9.651E-03
26	4.598E+15	7.898E-01	3.457E-02	7.499E-05	9.543E-03
HOLDER	FLUX	234U	235U	236U	90SR
8	3.065E+15	1.839E-02	3.246E-03	1.896E-03	5.396E-03
13	3.576E+15	2.093E-02	3.788E-03	2.681E-03	6.414E-03
21	4.366E+15	2.406E-02	4.467E-03	4.051E-03	7.981E-03
29	4.505E+15	2.452E-02	4.568E-03	4.307E-03	8.255E-03
26	4.598E+15	2.481E-02	4.632E-03	4.479E-03	8.439E-03
HOLDER	FLUX	95Zr	106Ru	137Cs	144Ce
8	3.065E+15	3.103E-03	2.070E-04	5.498E-03	3.430E-03
13	3.576E+15	3.686E-03	2.510E-04	6.558E-03	4.107E-03
21	4.366E+15	4.587E-03	3.215E-04	8.201E-03	5.164E-03
29	4.505E+15	4.746E-03	3.342E-04	8.492E-03	5.352E-03
26	4.598E+15	4.852E-03	3.427E-04	8.685E-03	5.477E-03
HOLDER	FLUX	125Sb	FIMA		
8	3.065E+15	7.695E-05	8.239E-02		
13	3.576E+15	8.953E-05	9.856E-02		
21	4.366E+15	1.079E-04	1.238E-01		
29	4.505E+15	1.110E-04	1.283E-01		
26	4.598E+15	1.131E-04	1.312E-01		

Table B.5. Calculated fission product in Biso-coated thoria particles from irradiation capsule HT-15
(atoms per initial atom of thorium)

HOLDER	FLUX	232TH	233PA	234PA	233U
8	3.065E+15	8.322E-01	2.668E-02	4.223E-05	1.140E-02
13	3.576E+15	8.072E-01	2.906E-02	5.201E-05	1.060E-02
21	4.366E+15	7.699E-01	3.197E-02	6.671E-05	9.495E-03
29	4.505E+15	7.635E-01	3.241E-02	6.921E-05	9.315E-03
26	4.598E+15	7.592E-01	3.268E-02	7.087E-05	9.197E-03
HOLDER	FLUX	234U	235U	236U	90SR
8	3.065E+15	1.975E-02	3.588E-03	2.579E-03	6.737E-03
13	3.576E+15	2.205E-02	4.085E-03	3.561E-03	7.953E-03
21	4.366E+15	2.469E-02	4.667E-03	5.209E-03	9.801E-03
29	4.505E+15	2.506E-02	4.749E-03	5.509E-03	1.012E-02
26	4.598E+15	2.529E-02	4.800E-03	5.710E-03	1.034E-02
HOLDER	FLUX	95ZR	106RU	137CS	144CE
8	3.065E+15	3.521E-03	2.559E-04	6.883E-03	4.184E-03
13	3.576E+15	4.149E-03	3.083E-04	8.156E-03	4.974E-03
21	4.366E+15	5.105E-03	3.910E-04	1.011E-02	6.190E-03
29	4.505E+15	5.271E-03	4.058E-04	1.045E-02	6.404E-03
26	4.598E+15	5.382E-03	4.156E-04	1.068E-02	6.546E-03
HOLDER	FLUX	125SB	FIMA		
8	3.065E+15	9.463E-05	1.034E-01		
13	3.576E+15	1.093E-04	1.229E-01		
21	4.366E+15	1.304E-04	1.529E-01		
29	4.505E+15	1.340E-04	1.582E-01		
26	4.598E+15	1.364E-04	1.617E-01		

Table B.6. Fission product inventories in Biso-coated ThO₂ particles from irradiation capsule HT-12, calculated for various neutron flux levels (atoms per initial atom of thorium)

FLUX	232TH	233PA	234PA	233U
2.7000E+15	9.6172E-01	2.0010E-02	2.8411E-05	7.0332E-03
3.0000E+15	9.5756E-01	2.1867E-02	3.3858E-05	7.2329E-03
3.3000E+15	9.5342E-01	2.3659E-02	3.9565E-05	7.3788E-03
3.6000E+15	9.4929E-01	2.5388E-02	4.5490E-05	7.4800E-03
3.9000E+15	9.4519E-01	2.7056E-02	5.1599E-05	7.5442E-03
4.2000E+15	9.4110E-01	2.8666E-02	5.7860E-05	7.5778E-03
4.5000E+15	9.3702E-01	3.0219E-02	6.4244E-05	7.5861E-03
4.8000E+15	9.3297E-01	3.1717E-02	7.0726E-05	7.5737E-03
5.1000E+15	9.2893E-01	3.3162E-02	7.7282E-05	7.5443E-03
5.4000E+15	9.2491E-01	3.4555E-02	8.3891E-05	7.5010E-03
FLUX	234U	235U	236U	90SR
2.7000E+15	3.7505E-03	3.7855E-04	3.9853E-05	4.7309E-04
3.0000E+15	4.4426E-03	4.7785E-04	5.6634E-05	5.5899E-04
3.3000E+15	5.1606E-03	5.8628E-04	7.7413E-05	6.4871E-04
3.6000E+15	5.8992E-03	7.0280E-04	1.0249E-05	7.4185E-04
3.9000E+15	6.6538E-03	8.2636E-04	1.3212E-05	8.3814E-04
4.2000E+15	7.4201E-03	9.5595E-04	1.6652E-04	9.3732E-04
4.5000E+15	8.1944E-03	1.0906E-03	2.0585E-04	1.0392E-03
4.8000E+15	8.9734E-03	1.2295E-03	2.5026E-04	1.1436E-03
5.1000E+15	9.7543E-03	1.3718E-03	2.9983E-04	1.2504E-03
5.4000E+15	1.0534E-02	1.5167E-03	3.5464E-04	1.3596E-03
FLUX	95ZR	106RU	137CS	144CE
2.7000E+15	3.8451E-04	1.7972E-05	4.7517E-04	3.2271E-04
3.0000E+15	4.5467E-04	2.1380E-05	5.6191E-04	3.8202E-04
3.3000E+15	5.2805E-04	2.4982E-05	6.5262E-04	4.4425E-04
3.6000E+15	6.0438E-04	2.8767E-05	7.4694E-04	5.0918E-04
3.9000E+15	6.8345E-04	3.2729E-05	8.4457E-04	5.7664E-04
4.2000E+15	7.6508E-04	3.6860E-05	9.4529E-04	6.4649E-04
4.5000E+15	8.4911E-04	4.1155E-05	1.0489E-03	7.1862E-04
4.8000E+15	9.3544E-04	4.5711E-05	1.1553E-03	7.9293E-04
5.1000E+15	1.0240E-03	5.0226E-05	1.2642E-03	8.6935E-04
5.4000E+15	1.1146E-03	5.4992E-05	1.3757E-03	9.4781E-04
FLUX	125SB	FIMA		
2.7000E+15	7.2803E-06	7.0361E-03		
3.0000E+15	8.5603E-06	8.3275E-03		
3.3000E+15	9.8815E-06	9.6801E-03		
3.6000E+15	1.1236E-05	1.1089E-02		
3.9000E+15	1.2619E-05	1.2550E-02		
4.2000E+15	1.4024E-05	1.4060E-02		
4.5000E+15	1.5449E-05	1.5616E-02		
4.8000E+15	1.6888E-05	1.7216E-02		
5.1000E+15	1.8341E-05	1.8859E-02		
5.4000E+15	1.9804E-05	2.0542E-02		

Table B.7. Fission product inventories in Biso-coated ThO₂ particles from irradiation capsule HT-13, calculated for various neutron flux levels (atoms per initial atom of thorium)

FLUX	232TH	233PA	234PA	233U
2.7000E+15	9.171%E-01	2.4275E-02	2.8900E-05	1.2615E-02
3.0000E+15	9.0838E-01	2.6184E-02	3.4216E-05	1.2532E-02
3.3000E+15	8.9969E-01	2.7969E-02	3.9718E-05	1.2406E-02
3.6000E+15	8.9109E-01	2.9637E-02	4.5363E-05	1.2251E-02
3.9000E+15	8.8257E-01	3.1195E-02	5.1111E-05	1.2077E-02
4.2000E+15	8.7413E-01	3.2649E-02	5.6928E-05	1.1892E-02
4.5000E+15	8.6577E-01	3.4005E-02	6.2783E-05	1.1699E-02
4.8000E+15	8.5749E-01	3.5270E-02	6.8650E-05	1.1501E-02
5.1000E+15	8.4929E-01	3.6448E-02	7.4504E-05	1.1302E-02
5.4000E+15	8.4116E-01	3.7544E-02	8.0325E-05	1.1103E-02
FLUX	234U	235U	236U	90SR
2.7000E+15	1.0924E-02	1.6305E-03	4.4194E-04	2.1889E-03
3.0000E+15	1.2469E-02	1.9300E-03	5.9427E-04	2.5099E-03
3.3000E+15	1.3976E-02	2.2289E-03	7.7074E-04	2.8351E-03
3.6000E+15	1.5435E-02	2.5235E-03	9.7064E-04	3.1642E-03
3.9000E+15	1.6839E-02	2.8112E-03	1.1929E-03	3.4968E-03
4.2000E+15	1.8181E-02	3.0897E-03	1.4365E-03	3.8327E-03
4.5000E+15	1.9458E-02	3.3575E-03	1.6998E-03	4.1716E-03
4.8000E+15	2.0668E-02	3.6136E-03	1.9815E-03	4.5134E-03
5.1000E+15	2.1809E-02	3.8571E-03	2.2800E-03	4.8579E-03
5.4000E+15	2.2881E-02	4.0876E-03	2.5938E-03	5.2048E-03
FLUX	95ZR	106RU	137CS	144CE
2.7000E+15	1.4895E-03	8.3213E-05	2.2117E-03	1.4358E-03
3.0000E+15	1.7077E-03	9.6397E-05	2.5397E-03	1.6525E-03
3.3000E+15	1.9295E-03	1.1002E-04	2.8729E-03	1.8738E-03
3.6000E+15	2.1546E-03	1.2407E-04	3.2110E-03	2.0996E-03
3.9000E+15	2.3829E-03	1.3852E-04	3.5536E-03	2.3296E-03
4.2000E+15	2.6142E-03	1.5337E-04	3.9005E-03	2.5636E-03
4.5000E+15	2.8484E-03	1.6860E-04	4.2515E-03	2.8013E-03
4.8000E+15	3.0852E-03	1.8419E-04	4.6064E-03	3.0427E-03
5.1000E+15	3.3247E-03	2.0013E-04	4.9649E-03	3.2875E-03
5.4000E+15	3.5664E-03	2.1639E-04	5.3268E-03	3.5354E-03
FLUX	125SB	FIMA		
2.7000E+15	3.2769E-05	3.2935E-02		
3.0000E+15	3.7203E-05	3.7878E-02		
3.3000E+15	4.1596E-05	4.2919E-02		
3.6000E+15	4.5940E-05	4.8050E-02		
3.9000E+15	5.0234E-05	5.3268E-02		
4.2000E+15	5.4476E-05	5.8570E-02		
4.5000E+15	5.8666E-05	6.3952E-02		
4.8000E+15	6.2806E-05	6.9411E-02		
5.1000E+15	6.6895E-05	7.4944E-02		
5.4000E+15	7.0936E-05	8.0547E-02		

Table B.8. Fission product inventories in Biso-coated ThO₂ particles from irradiation capsule HT-14, calculated for various neutron flux levels (atoms per initial atom of thorium)

FLUX	232TH	233PA	234PA	233U
2.7000E+15	8.7064E-01	2.5711E-02	3.6682E-05	1.2016E-02
3.0000E+15	8.5734E-01	2.7489E-02	4.2764E-05	1.1593E-02
3.3000E+15	8.4424E-01	2.9109E-02	4.8901E-05	1.1178E-02
3.6000E+15	8.3135E-01	3.0583E-02	5.5041E-05	1.0776E-02
3.9000E+15	8.1865E-01	3.1923E-02	6.1140E-05	1.0388E-02
4.2000E+15	8.0615E-01	3.3138E-02	6.7162E-05	1.0015E-02
4.5000E+15	7.9383E-01	3.4237E-02	7.3077E-05	9.6570E-03
4.8000E+15	7.8171E-01	3.5229E-02	7.8862E-05	9.3148E-03
5.1000E+15	7.6977E-01	3.6122E-02	8.4497E-05	8.9874E-03
5.4000E+15	7.5801E-01	3.6923E-02	8.9966E-05	8.6743E-03
FLUX	234U	235U	236U	90SR
2.7000E+15	1.6326E-02	2.8102E-03	1.4012E-03	4.6670E-03
3.0000E+15	1.8040E-02	3.1708E-03	1.8028E-03	5.2656E-03
3.3000E+15	1.9610E-02	3.5048E-03	2.2440E-03	5.8638E-03
3.6000E+15	2.1037E-02	3.8108E-03	2.7194E-03	6.4612E-03
3.9000E+15	2.2325E-02	4.0890E-03	3.2235E-03	7.0576E-03
4.2000E+15	2.3477E-02	4.3397E-03	3.7510E-03	7.6523E-03
4.5000E+15	2.4500E-02	4.5641E-03	4.2970E-03	8.2450E-03
4.8000E+15	2.5402E-02	4.7633E-03	4.8567E-03	8.8352E-03
5.1000E+15	2.6191E-02	4.9390E-03	5.4258E-03	9.4224E-03
5.4000E+15	2.6875E-02	5.0926E-03	6.0004E-03	1.0006E-02
FLUX	95ZR	106RU	137CS	144CE
2.7000E+15	2.6872E-03	1.7633E-04	4.7432E-03	2.9511E-03
3.0000E+15	3.0286E-03	2.0141E-04	5.3625E-03	3.3438E-03
3.3000E+15	3.3707E-03	2.2702E-04	5.9838E-03	3.7398E-03
3.6000E+15	3.7133E-03	2.5311E-04	6.6067E-03	4.1384E-03
3.9000E+15	4.0559E-03	2.7963E-04	7.2308E-03	4.5391E-03
4.2000E+15	4.3983E-03	3.0652E-04	7.8556E-03	4.9414E-03
4.5000E+15	4.7400E-03	3.3374E-04	8.4805E-03	5.3447E-03
4.8000E+15	5.0805E-03	3.6123E-04	9.1050E-03	5.7483E-03
5.1000E+15	5.4194E-03	3.8895E-04	9.7285E-03	6.1517E-03
5.4000E+15	5.7563E-03	4.1683E-04	1.0350E-03	6.5543E-03
FLUX	125SB	FIMA		
2.7000E+15	6.7590E-05	7.1061E-02		
3.0000E+15	7.5296E-05	8.0522E-02		
3.3000E+15	8.2794E-05	9.0060E-02		
3.6000E+15	9.0094E-05	9.9669E-02		
3.9000E+15	9.7206E-05	1.0934E-01		
4.2000E+15	1.0414E-04	1.1907E-01		
4.5000E+15	1.1090E-04	1.2884E-01		
4.8000E+15	1.1750E-04	1.3865E-01		
5.1000E+15	1.2394E-04	1.4848E-01		
5.4000E+15	1.3023E-04	1.5833E-01		

Table B.9. Fission product inventories in Biso-coated ThO₂ particles from irradiation capsule HT-15, calculated for various neutron flux levels (atoms per initial atom of thorium)

FLUX	232TH	233PA	234PA	233U
2.7000E+15	8.5067E-01	2.4707E-02	3.5244E-05	1.2008E-02
3.0000E+15	8.3552E-01	2.6345E-02	4.0976E-05	1.1508E-02
3.3000E+15	8.2064E-01	2.7823E-02	4.6732E-05	1.1027E-02
3.6000E+15	8.0602E-01	2.9156E-02	5.2462E-05	1.0568E-02
3.9000E+15	7.9167E-01	3.0355E-02	5.8124E-05	1.0130E-02
4.2000E+15	7.7757E-01	3.1429E-02	6.3686E-05	9.7153E-03
4.5000E+15	7.6372E-01	3.2390E-02	6.9120E-05	9.3215E-03
4.8000E+15	7.5012E-01	3.3245E-02	7.4405E-05	8.9481E-03
5.1000E+15	7.3676E-01	3.4002E-02	7.9523E-05	8.5940E-03
5.4000E+15	7.2364E-01	3.4670E-02	8.4461E-05	8.2582E-03
FLUX	234U	235U	236U	90SR
2.7000E+15	1.7793E-02	3.1684E-03	1.9430E-03	5.8597E-03
3.0000E+15	1.9418E-02	3.5164E-03	2.4606E-03	6.5805E-03
3.3000E+15	2.0866E-02	3.8287E-03	3.0183E-03	7.2971E-03
3.6000E+15	2.2142E-02	4.1060E-03	3.6082E-03	8.0089E-03
3.9000E+15	2.3256E-02	4.3499E-03	4.2226E-03	8.7154E-03
4.2000E+15	2.4220E-02	4.5624E-03	4.8546E-03	9.4160E-03
4.5000E+15	2.5045E-02	4.7456E-03	5.4978E-03	1.0110E-02
4.8000E+15	2.5742E-02	4.9020E-03	6.1464E-03	1.0797E-02
5.1000E+15	2.6324E-02	5.0339E-03	6.7954E-03	1.1477E-02
5.4000E+15	2.6800E-02	5.1435E-03	7.4403E-03	1.2149E-02
FLUX	95ZR	106RU	137CS	144CE
2.7000E+15	3.0680E-03	2.1914E-04	5.9695E-03	3.6201E-03
3.0000E+15	3.4400E-03	2.4923E-04	6.7191E-03	4.0827E-03
3.3000E+15	3.8102E-03	2.7978E-04	7.4675E-03	4.5463E-03
3.6000E+15	4.1783E-03	3.1073E-04	8.2142E-03	5.0101E-03
3.9000E+15	4.5439E-03	3.4199E-04	8.9585E-03	5.4735E-03
4.2000E+15	4.9063E-03	3.7351E-04	9.6997E-03	5.9355E-03
4.5000E+15	5.2651E-03	4.0520E-04	1.0437E-02	6.3956E-03
4.8000E+15	5.6199E-03	4.3701E-04	1.1170E-02	6.8530E-03
5.1000E+15	5.9702E-03	4.6887E-04	1.1898E-02	7.3070E-03
5.4000E+15	6.3157E-03	5.0073E-04	1.2621E-02	7.7570E-03
FLUX	125SB	FIMA		
2.7000E+15	8.3633E-05	8.9676E-02		
3.0000E+15	9.2688E-05	1.0119E-01		
3.3000E+15	1.0145E-04	1.1275E-01		
3.6000E+15	1.0994E-04	1.2434E-01		
3.9000E+15	1.1816E-04	1.3596E-01		
4.2000E+15	1.2614E-04	1.4759E-01		
4.5000E+15	1.3387E-04	1.5921E-01		
4.8000E+15	1.4139E-04	1.7082E-01		
5.1000E+15	1.4868E-04	1.8241E-01		
5.4000E+15	1.5577E-04	1.9396E-01

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